Studies in the Analytical Chemistry of Molybdenum and Vanadium

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I. THE VOLATILITY OF MOLYBDENUM TRIOXIDE

II. THE SEPARATION OF MOLYBDENUM FROM VANADIUM AS SULPHIDE.

III. AN IODOMETRIC METHOD FOR THE DETERMINATION OF VANADIUM.

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

L. C.

BY

ARTHUR EDWARD STOPPEL

MAY, 1924

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STUDIES IN THE ANALYTICAL CHEMISTRY OF MOLYBDENUM AND VANADIUM

I. The Volatility of Molybdenum Trioxide.

II. The Separation of Molybdenum from Vanadium as Sulphide.

III. An Iodometric Method for the Determination of Vanadium.

Introductory

The increasing use of molybdenum and vanadium in the industries has demanded accurate methods for their determination. The fact that these two elements occur together not only in nature, but also in manufactured products such as the alloy steels, makes it necessary to be able to make a correct estimation of either one in the presence of the other. This is often a difficult problem, as both have many reactions in common, and they are therefore difficult to separate. This, coupled with the fact that the literature on the subject is contradictory, makes it desirable to attempt to clear up some of the disputed points, and to determine, if possible, the best methods for the analytical separation of these two elements.

To attempt to include all of the work that has been published on the analytical chemistry of molybdenum and vanadium is beyond the scope of this paper. Most of the proposed methods will be mentioned only briefly. A discussion of the analytical chemistry of vanadium will be taken up first, followed by a similar discussion of molybdenum, after which some of the proposed methods for the separation will be mentioned. A fuller discussion of some of the points investigated in this research will be given in the experimental part of this paper.

There are several delicate tests used to show the qualitative presence of vanadium, and to estimate small quantities of it colorimetrically. The most common of these depends on the reddish-brown coloration given to strongly acid vanadium solutions by hydrogen peroxide. The method was suggested by Maillard[1] who used a solution of hydrogen peroxide in ether as the reagent. Later modifications as applied to steel analysis are described by Slavik[2], Pickard[3], and others. Gregory's[4] method depends upon the coloration given to a solution of vanadic acid in concentrated sulphuric acid by a solution of strychnine in concentrated sulphuric acid. A violet coloration first appears, which changes rapidly to a more permanent orange. The coloration is proportional to the amount of vanadium present, so it may be made the basis of a colorimetric method. A very delicate test is due to Maurio[5], who applied it to the determination of small amounts of vanadium in water. The reagent, a dilute solution of diphenylamine in water, when added to a strong hydrochloric acid solution of the water to be tested, gives a violet coloration in the presence of vanadium. The test is more delicate than the hydrogen peroxide test. Cupferron is also said to show the presence of very small amounts of vanadium[6].

[1] Chem. News 82, 19 (1900).
[2] Chem. Ztg. 34, 648 (1909).
[3] Chem. World (2) 341 (1914).
[4] Chem. News 100, 221 (1909).
6 C. A. 9, 2201 (1915).
5 ~~Rodeja~~. C. A. 12, 1221 (1918).

In its gravimetric determination, vanadium is usually weighed as V_2O_5, resulting from the ignition of mercurous vanadate, ammonium meta-vanadate, or the precipitate obtained with cupferron.

Vanadium is completely precipitated from neutral solutions by mercurous nitrate. The precipitate on ignition is converted to V_2O_5, in which form it is weighed. Molybdenum interferes as it is also quantitatively precipitated under these conditions.

The lead acetate method of Roscoe[7] is said to be very satisfactory. When lead acetate is added to a slightly acetic acid solution of a vanadate, all of the vanadium is precipitated as basic lead vanadate. Owing to the variable composition of the precipitate, it cannot be ignited and weighed as such, but the lead must first be converted into sulphide or sulphate, and removed by filtration. The fiiltrate containing the vanadium is evaported to dryness, and the residue is ignited to V_2O_5.

When a concentrated slightly ammoniacal solution of a vanadate is saturated with ammonium chloride, the vanadium is precipitated as ammonium meta-vanadate. Upon ignition this is converted to V_2O_5. This method has been the subject of considerable controversy in the literature. It originated with Berzelius-Hauer[8]. Ditte[9] added alcohol to obtain complete precipitation. Holverscheit[10] obtained low results with the method, as did Roscoe, Rosenheim, Milch, and others. Gooch and Gilbert[11] obtained satisfactory results when using pure solutions.

Browning and Palmer[12] precipitated vanadic acid from neutral solution by means of silver nitrate. The precipitate after gentle ignition is weighed as $AgVO_3$.

Carnot[13] suggests three methods for the determination of vanadium. Vanadates are precipitated from boiling slightly ammoniacal solutions containing excess ammonium chloride by manganous chloride or manganous sulphate. The precipitate, on ignition, is converted to $Mn_2V_2O_7$. By adding an excess of barium chloride to the neutral or slightly ammoniacal solution of a vanadate, and boiling, a white precipitate is obtained, which on ignition becomes $Ba_2V_2O_7$. According to Beard[14], accurate results are possible only by redissolving the precipitate, removing the barium by treating with sulphuric acid and filtering, evaporating the filtrate to dryness, and igniting to V_2O_5. Uranyl nitrate, when added to an acetic acid solution of a vanadate containing considerable alkali acetate, precipitates the vanadium as a yellow precipitate, resembling arsenious sulphide in appearance. The precipitate may be dried at 100° and weighed as $2UO_3(NH_4)_2O.V_2O_5.H_2O$, or it may be ignited to redness and weighed as $2UO_3.V_2O_5$.

According to Turner[15] vanadium is completely precipitated from a one per cent hydrochloric or sulphuric acid solution by means of cupferron. The precipitate is ignited to V_2O_5.

[7] Ann. Chem. Pharm. Suppl. 8, 102 (1872).
[8] Jour. Prakt. Chem. 69, 385 (1856).
[9] Chem. News 55, 203 (1887).
[10] Inaug. Diss. Berlin (1890).
[11] Am. J. Sci. (4) 14, 205 (1902).
[12] Am. J. Sci. (4) 30, 220 (1910).
[13] Chem. News 56, 16-42 (1887).
[14] Ann. Chim. anal. chim. appl. 10, 41 (1905).
[15] Am. J. Sci. (4) 29, 540 (1910).

When a solution of a vanadate, slightly acid with sulphuric acid, is boiled with electrolytic silver[16], the vanadium is reduced to the vanadyl condition, and an equivalent amount of silver is dissolved. The amount of vanadium present may then be estimated in three different ways: first, from the loss in weight of the metallic silver; second, by titrating the reduced vanadyl solution with standard potassium permanganate; and third, by titrating the dissolved silver with a standard thiocyanate solution.

Perkins[17] found that when an acid solution of a vanadate was shaken with potassium iodide and electrolytic silver, the vanadium was reduced to the vanadyl condition, and the iodine liberated combined with the silver present to form silver iodide. The following reactions take place.

$$V_2O_5 + 2I^- + 2H^+ = V_2O_4 + I_2 + H_2O.$$
$$I_2 + 2Ag = 2AgI.$$

Molybdenum, selenium, and tellurium give similar recations.

By heating a sulphuric acid solution of a vanadate with oxalic acid, the vanadium is reduced to the vanadyl state, liberating a corresponding amount of carbon dioxide, which may be absorbed in caustic potash and weighed[18]. Molybdenum does not interfere.

Truchot[19] uses an electrolytic method, by electrolyzing a hot slightly ammoniacal solution with a current of 0.3 amperes at 2 to 2.5 volts for 8 or 10 hours. The lower oxide that deposits on the electrode is ignited and weighed as V_2O_5. Molybdenum is deposited under the same conditions. On ignition it is converted to MoO_3, which melts and volatilizes completely at redness. In case of a mixture of molybdenum and vanadium, the precipitate is first ignited gently and weighed, giving $V_2O_5 + MoO_3$; then heated to redness to constant weight which gives the V_2O_5. The MoO_3 may be determined by difference.

Volumetric methods for the determination of vanadium are usually preferred to the gravimetric, because of their shortness as well as their probable greater accuracy. The most common volumetric methods depend on the reduction of vanadium to one of the lower oxides, followed by oxidation with standard permanganate. The titration is usually made in a hot (60°) solution containing sulphuric acid.

Vanadates may be reduced to vanadyl compounds by a number of reagents. Sulphur dioxide[20] and hydrogen sulphide[21] may be used, the excess being expelled by boiling. Campagne[22] evaporates the solution to low volume with concentrated hydrochloric acid. It is said that the presence of ferric iron aids the reduction. Muller and Diefenthaler[23] reduce by evaporating with hydrochloric acid and alcohol. Hensen[24] adds a little oxalic acid and bring to fumes of sulphur trioxide. Cain and Hostetter[25] have shown that hydrogen peroxide and persulphates reduce vanadium when added to a concentrated sulphuric acid solution of the vanadium.

[16] Edgar, J. Am. Chem. Soc. 38, 1297 (1916).
[17] Am. J. Sci. (4) 29, 542 (1910).
[18] Rosenheim and Friedheim. Chem. News 66, 27 (1892).
[19] Ann. chim. anal. chim. appl. 7, 165 (1902).
[20] Hillebrand. J. Am. Chem. Soc. 20, 462 (1898).
[21] Lundell and Knowles. J. Am. Chem. Soc. 43, 1560 (1921).
[22] Ber. 36, 3167 (1903).
[23] Z. anorg. Chem. 71, 343 (1911).
[24] Inaug. Diss. Aachen (1909).
[25] J. Am. Chem. Soc. 34, 274 (1912).

Bleecker[26] electrolyses the sulphuric acid solution containing copper sulphate for 10 minutes, and finds complete reduction to V_2O_4. McCay and Anderson[27] reduce by shaking the hydrochloric or sulphuric acid solution with metallic mercury. Edgar[16] found complete reduction by boiling the acid solution with metallic silver. Gooch and Gilbert[28] pass the warm sulphuric acid solution through a column of zinc. This reduces the vanadium below the vanadyl state, and oxidation to this point is brought about by adding silver sulphate. All of these methods leave the vanadium in the tetravalent condition, and it is oxidized to the pentavalent condition standard permanganate.

Vanadium may be reduced to the divalent state by passing the warm acid solution through a column of amalgamated zinc. Gooch and Edgar[29] obtained good results with this method by catching the reduced solution in a solution of ferric alum and titrating with permanganate. They found the method of Glasman[30] (reduction with metallic magnesium to V_2O_3) to give irregular results.

Vanadates may be titrated directly using standard reducing agents. Lindeman[31] titrates with ferrous sulphate using potassium ferricyanide as an outside indicator. Johnson[32] utilizes the same method in steel analysis, but uses the indicator internally. Another variation is that of Kelly and Conant[33] who employ an electrometric end point. Warynsky and Mdivani[34] use stannous chloride as the reducing solution, using an outside indicator of ammonium molybdate. Reduction goes to the vanadyl state. Travers[35] reduces vanadium by adding titanous chloride. The excess titanous chloride is then titrated with ferric chloride using potassium thiocyanate as indicator. Molybdenum may be estimated by a similar method. Attack[36] reduces the vanadate to vanadyl with an excess of methylene white, and titrates the resulting methylene blue with titanous chloride.

Oberhelman[37] reduces the vanadate with a slight excess of sodium thiosulphate, using copper sulphate as a catalyst. The excess thiosulphate is finally oxidized with standard iodine solution.

Palmer[38] oxidizes tetravalent vanadium in alkaline solution with potassium ferricyanide, and titrates the potassium ferrocyanide formed with permanganate in acid solution.

Edgar[39] makes use of an indirect method. He adds an excess of standard silver nitrate to the vanadate such that Ag_3VO_4 is precipitated. The excess silver in the filtrate is estimated by Volhard's thiocyanate titration.

There are also a number of iodometric methods. A very accurate one is due to Holverscheit[10], which consists of distilling a vanadate with concentrated hydro-

[26] Met. Chem. Eng. 9, 209 (1911).
[27] J. Am. Chem. Soc. 44, 1018 (1922).
[28] Chem. News 87, 265 (1903).
[29] Chem. News 98, 2 (1908).
[30] Ber. 38, 600 (1905).
[31] Z. anal. Chem. 18, 99 (1879).
[32] Chem. Analysis of Special Steels, Steel-making Alloys, and Graphites. 1920, p. 6, John Wiley and Sons.
[33] J. Am. Chem. Soc. 38, 341 (1916).
[34] Bull. soc. chim. (4) 3, 626 (1908).
[35] Compt. rend. 165, 362 (1917).
[36] Analyst 38, 99 (1913).
[37] Chem. News 113, 87 (1916).
[38] Am. J. Sci. (4) 30, 141 (1910).
[39] Am. Chem. J. 44, 467 (1910).

chloric acid and a little potassium bromide. The vanadate is reduced to vanadyl, the bromine liberated being absorbed in potassium iodide solution, and estimated by titration with standard thiosulphate. By using potassium iodide instead of potassium bromide, and phosphoric acid instead of hydrochloric acid, Friedheim and Euler[40] found it possible to reduce the vanadium to V_2O_3 by boiling to a very low volume.

Ditz and Bardach[41] reduce in the cold using potassium bromide and a large excess of concentrated hydrochloric acid. After standing for some time, the solution is diluted, and the bromine liberated is determined iodometrically. Muller and Diefenthaler[42] reduce the vanadium with potassium ferrocyanide. The resulting ferricyanide is treated with potassium iodide, and the iodine liberated is titrated with thiosulphate.

Browning and Goodman[43] reduce vanadates to vanadyl by boiling their solutions with tartaric, oxalic, or citric acid. The cooled solution is then treated with an excess of potassium bicarbonate, and the vanadium is reoxidized by adding an excess of standard iodine. After considerable standing in a dark place, the excess iodine is bleached with standard arsenite solution. If the proper precautions are taken, molybdenum and tungsten do not interfere. Browning[44] uses the same method except that the reduction is brought about by boiling the sulphuric acid solution with 1 or 1.5 grams of potassium iodide or bromide. After cooling, the solution is treated with potassium bicarbonate, and the titration is made as before.

Review of Methods for the Determination of Molybdenum.

One of the most delicate tests for molybdenum is due to the red color resulting when reduced molybdenum solution is treated with thiocyanate. The test is usually made by treating the hydrochloric acid solution suspected of containing molybdenum with potassium or ammonium thiocyanate, and adding a few pieces of zinc. If molybdenum is present, a cherry-red color will soon develop. Stannous chloride may be substituted for the zinc. The test may be made still more sensitive by shaking the solution with ether, in which the colored compound is soluble.

Another delicate test is the blue coloration obtained when an acetic acid solution of a molybdate is treated with hydrazine sulphate. When an almost neutral solution is treated with xanthic acid or the potassium salt of this acid, and acidified with a few drops of strong acid, a yellowish cloudiness appears[45], which changes to red and then violet, unless the amount of molybenum present is small, when the color remains red. More than traces of molybdenum cause the formation of black oily drops. The color is soluble in ether, carbon disulphide, and chloroform. Under favorable conditions, the test is sensitive to 0.00064 mg. of molybdenum per c. c.

Gravimetrically molybdenum is usually weighed as lead molybdate, or in some form resulting from the ignition of the sulphide.

The precipitation of molybdenum as sulphide by means of hydrogen sulphide in acid solution is complete only when pressure is used, according to a number of investigators[46], although Sterba-Bohm and Vestrebal[47] found complete precipitation

[40] Ber. 28, 2067 (1895).
[41] Z. anorg. Chem. 93, 97 (1915).
[42] Z. anal. Chem. 51, 21 (1912).
[43] Z. anorg. Chem. 13, 427 (1897).
[44] Am. J. Sci. (4) 2, 185 (1896).
[45] Chem. Ztg. 43, 777 (1919).
[46] Dohler. Chem. News. 82, 294 (1900).
[47] Z. anorg. Chem. 110, 81 (1920).

by passing the gas into a solution acidified with formic acid without using increased pressure. To avoid the use of a pressure flask, the precipitation is sometimes made by acidifying the ammoniacal solution that has been saturated with hydrogen sulphide. This usually precipitates all but traces of the molybdenum. Low[48] states that if the passage of hydrogen sulphide is continued for about 15 minutes after the acidification, all of the molybdenum will come down with one precipitation. The precipitate may be dried at 250° C. in an atmosphere of carbon dioxide, and weighed as MoS_3, according to Sterba-Bohm and Vestrebal[47]. It may be gently ignited in the air to MoO_3, or it may be treated with sulphur and ignited over hydrogen in a Rose crucible to MoS_2[49]. Other investigators have suggested dissolving the precipitate, and reprecipitating it as lead molybdate[48], or estimating the molybdenum by a volumetric method, such as titration with lead acetate, or by reducing it with zinc and titrating with permanganate.

The precipitation of molybdenum as lead molybdate was first suggested by Chatard[50]. The method was developed by Brearley[51] who found precipitation to be complete in weak acetic acid solutions, containing alkali acetate. Weiser[52] found that the physical characteristics of the precipitate could be improved considerably by using lead nitrate instead of lead acetate, or using the latter in the presence of a little free nitric acid, and finally neutralizing the solution with ammonium hydroxide.

Molybdenum may be precipitated as mercurous molybdate in neutral solution by mercurous nitrate. The precipitate is converted to MoO_3 by gentle ignition, or it may be reduced to metallic molybdenum by heating over a blast lamp in a current of hydrogen[53].

By treating a neutral solution of a molybdate with barium chloride, and heating to boiling, barium molybdate is precipitated, and after ignition is weighed as such[54].

When an acid solution of a molybdate is shaken with potassium iodide and electrolytic silver, the molybdenum is reduced to Mo_2O_5, and the liberated iodine combines with the silver to form silver iodide[17].

The most reliable volumetric method for the determination of molybdenum depends upon the reduction of MoO_3 to Mo_2O_3 by zinc. Randall[55] has shown that the method is satisfactory when the warm sulphuric acid solution of the molybdate is passed through a Jones reductor, and caught in a solution of ferric alum. Titration is then made with standard permanganate. Instead of catching the solution in ferric alum, Jamieson[56] catches the reduced solution in iodine monochloride, and titrates with potassium iodate, the molybdenum becoming oxidized to Mo_2O_5 under these conditions. This last titration must be performed in the presence of considerable hydrochloric acid, to prevent the hydrolysis of iodine monochloride formed during the reaction.

Titration of molybdates with lead acetate using tannic acid as outside indicator has been suggested.

[48] Technical Methods of Ore Analysis, 9th Edition, 1922, p. 162. John Wiley and Sons.
[49] Collett and Eckhardt. Chem. Ztg. 33, 968 (1909).
[50] Chem. News 24, 175 (1871).
[51] Chem. News 78, 203 (1898).
[52] J. Phys. Chem. 20, 640 (1916).
[53] Von der Pfordten. Chem. News 50, 18 (1884).
[54] Mennicke. Die quantitativen Untersuchungsmethoden des Molybdens, Vanadiums, und Wolframs. Berlin 1913. p. 19.
[55] Am. J. Sci. (4) 24, 313 (1907).
[56] J. Am. Chem. Soc. 39, 246 (1917).

Knecht and Attack[57] reduce with zinc and hydrochloric acid, and titrate with methylene blue, which oxidizes the moylbdenum to $MoCl_5$. Travers[25] treats a molybdate with excess titanous chloride, and titrates back with ferric chloride, using potassium thiocyanate as indicator. The method is not satisfactory for concentrations of molybdenum greater than 0.05 g. per liter, as Mo_2O_5 is oxidized by ferric chloride under these conditions. Willard and Fenwick[58] titrate with titanous chloride using an electrometric end point.

An iodometric distillation method has been proposed by Gooch and Fairbanks[59] by boiling the solution containing the molybdenum with hydrochloric acid and potassium iodide. The volumes must be kept within well defined limits, as the amount of iodine liberated depends upon the length of time the distillation has been carried on. High or low results may be obtained depending on these conditions. The iodine liberated may be caught in potassium iodide solution, and estimated by titration with standard thiosulphate. The reduction proceeds to Mo_2O_5 if the conditions are right. The reduced molybdenum may also be determined directly by treating with tartaric acid and an excess of sodium bicarbonate, and titrating with standard iodine. An excess of iodine must be added, and after 2 hours standing in a dark place, the excess is bleached with standard arsenite solution. Gooch and Pulman[60] give directions for a more rapid procedure, which consists of oxidizing the reduced solution with potassium permanganate, followed by a measured amount of standard arsenite. The solution is now treated with sodium bicarbonate and tartaric acid, and titrated to an immediate end point with iodine using starch as indicator.

Kollock and Smith[61] have shown that molybdenum is completely deposited electrolytically on the cathode from weak sulphuric, hydrochloric, or acetic acid solutions. Wherry and Smith[62] have introduced the application of the rotating anode to the above method. The lower oxide deposited is ignited at 400° and weighed as MoO_3.

Proposed Methods for the Separation of Molybdenum and Vanadium

Various methods for the separation of molybdenum and vanadium have been proposed from time to time. The one in almost universal use depends upon the precipitation of molybdenum sulphide in acid solution by means of hydrogen sulphide in a pressure flask[63]. A variation of this method consists in saturating the ammoniacal solution containing tartaric acid with hydrogen sulphide, and acidifying with sulphuric acid. The vanadium is said to remain in solution under both conditions.

Gibbs[64] has found that the precipitation of ammonium meta-vanadate from slightly ammoniacal solutions with ammonium chloride gives a quantitative separation of vanadium from molybdenum.

Carnot[13] claims his method of precipitating vanadates with manganous salts gives a complete separation from molybdenum, especially if the solution is not

[57] Analyst 36, 98 (1911).
[58] J. Am. Chem. Soc. 45, 928 (1923).
[59] Z. anorg. Chem. 13, 101 (1897).
[60] Am. J. Sci. (4) 12, 449 (1901).
[61] J. Am. Chem. Soc. 23, 669 (1901).
[62] J. Am. Chem. Soc. 29, 806 (1907).
[63] Treadwell and Hall, Analytical Chemistry. Vol. II. 5th ed., John Wiley and Sons, New York, 1919, p. 308.
[64] Am. Chem. J. 5 371 (1884).

boiled too long after the reagent has been added. Svensson[65] utilizes this reaction to make the separation in steel analysis, and finds it best to let the solution stand over night to insure complete precipitation of the vanadium.

By digesting the freshly precipitated lead salts of vanadium, molybdenum, phosphorous, arsenic, chromium, and tungsten with a saturated solution of potassium carbonate, T. Fisher[66] found lead vanadate to be unchanged, while the other lead salts were wholly decomposed.

Willard and Fenwick[68] make the separation by means of lead perchlorate in 2 per cent perchloric acid. The molybdenum precipitates as lead molybdate under these conditions while the vanadium remains in solution. They give data showing the separation of 5 mg. of vanadium from 72 mg. of molybdenum.

Blair[67] found that molybdenum follows the iron into the ether layer when an ether separation of iron from vanadium is made in steel analysis.

A rather unusual method has been proposed in case a mixture of V_2O_5 and MoO_3 is the weighing form. This condition might result in a number of ways; for instance, it would occur when the lower oxides of both metals, deposited by electrolysis[19], are ignited, or it might occur when the precipitate obtained with mercurous nitrate is ignited. In either case, gentle ignition will give the total V_2O_5 and MoO_3. If the mixture is then heated to redness until all the molybdenum has disappeared due to its greater volatility, the V_2O_5 remaining may be weighed, and the MoO_3 determined by difference. Or, according to the procedure of Gibbs[64], one portion of the precipitate may be ignited to redness to constant weight to get the V_2O_5 alone. Another portion is ignited with a weighed portion of sodium acid tungstate to redness. This prevents the loss of MoO_3, and gives the total MoO_3 and V_2O_5.

Meyers[68] has suggested an electrolytic method for the separation. The solution, containing 20 drops of concentrated sulphuric acid, is electrolysed with a current of 1.6 to 2 amperes at 6.5 volts, using a mercury cathode. It is best to neutralize part of the sulphuric acid with potassium hydroxide after all but the last traces of molybdenum are deposited. If the neutralization has been carried too far, an oxide of vanadium will deposit on the anode. If much vanadium is present, the molybdenum is incompletely deposited. For instance, when a solution containing 0.0095 g. molybdenum and 0.2 g. vanadium was electrolysed, the molybdenum could not be completely deposited.

Methods for the Determination of Vanadium in the Presence of Molybdenum

Besides actual separations, several methods have been proposed for the determination of vanadium in the presence of molybdenum. These are usually volumetric methods in which the vanadium is reduced by some reagent that does not affect the molybdenum, after which the vanadium is reoxidized by some standard oxidizing solution, usually permanganate.

The method of Cain and Hostetter[25] of reducing vanadates in concentrated sulphuric acid solution to vanadyl compounds by means of hydrogen peroxide, is performed in the presence of molybdenum. Campagne's method of reducing vanadium

[65] Stahl u. Eisen 28, 853 (1909).
[66] Inaug. Diss. Rostock 1894.
[67] J. Am. Chem. Soc. 30, 1229 (1908).
[68] J. Am. Chem. Soc. 26, 1130 (1904).

by evaporation with concentrated hydrochloric acid may be carried out in the presence of molybdenum[69]. Holverscheit's potassium bromide distillation method may also be carried out in the presence of molybdates.

Travers[70] titrates a mixture of the two elements with titanous chloride using potassium thiocyanate as indicator. The vanadium is all reduced to the vanadyl state, and the molybdenum is unchanged when a permanent vermillion tint appears.

Tartaric, citric, or oxalic acids will not reduce molybdenum, but reduce vanadium, as shown by Browning and Goodman[43]. The vanadium may be reoxidized with standard iodine after treating the reduced solution with sodium bicarbonate. If oxalic acid was used, the vanadium content may be obtained by absorbing and weighing the carbon dioxide liberated[18].

When sulphur dioxide is passed into a solution of a vanadate and a molybdate, only the vanadium is reduced providing there is sufficient sulphuric acid present. No molybdenum is reduced when 0.4 g. of MoO_3 is present with 5 c. c. of concentrated sulphuric acid in a volume of 25 c. c.[71].

Differential Methods for the Determination of Molybdenum and Vanadium

Several differential methods for the determination of vanadium and molybdenum may also be found in the literature.

The vanadium in a solution of both elements may first be determined by reduction with sulphur dioxide, expulsion of the excess sulphur dioxide by boiling, and titration of the vanadyl compound with permanganate as above[71]. The solution is then passed through a Jones reductor, caught in ferric alum, and titrated with permanganate. The first titration oxidizes V_2O_4 to V_2O_5. The second Oxidizes V_2O_2 to V_2O_5 and Mo_2O_3 to MoO_3. The permanganate used up by the molybdenum is therefore the second titration minus 3 times the first.

Glasman[30] reduces the mixture with metallic magnesium, and titrates with permanganate. He then reduces the solution with zinc and sulphuric acid, and again titrates with permanganate. He claims that magnesium reduces V_2O_5 to V_2O_2, and MoO_3 to Mo_2O_3; while zinc reduces V_2O_5 to V_2O_2, and MoO_3 to Mo_2O_3. From this data the amounts of vanadium and molybdenum present can be calculated. Gooch and Edgar[29] however, have shown that the action of magnesium on vanadium is irregular.

Friedheim and Euler[40] propose an iodometric distillation method. The mixture of the two acids is distilled in a Bunsen apparatus with potassium bromide and hydrochloric acid. The vanadium is reduced to vanadyl, and is estimated by titrating the bromine liberated. The solution remaining in the distilling flask is then treated with potassium iodide and sirupy phosphoric acid, and boiled until no more iodine is given off. This reduces the V_2O_4 to V_2O_3 and MoO_3 to Mo_2O_5. The iodine liberated is absorbed in potassium iodide solution and titrated with standard thiosulphate. Gooch and Fairbanks[59] have shown, however, that when the solution has been boiled sufficiently to reduce the vanadium to V_2O_3, the molybdenum is reduced a little farther than Mo_2O_5; consequently too much iodine is liberated, and too high a value is obtained for the molybdenum.

[69] Analytical Methods for Certain Metals. R. B. Moore, S. C. Lind, J. W. Warden, J. P. Bonardi, C. W. Davis, and J. E. Conley, Bur. of Mines, Bull. 212 (1923), p. 274.
[70] Compt. rend. 166, 289 (1918).
[71] Am. J. Sci. (4) 25, 332 (1908).

Travers[70] proposes the following method. Two aliquot parts of the solution are taken. In the first, vanadium only is determined by adding potassium thiocyanate indicator, and titrating to a rose color with titanous chloride as described above. In the second portion, the molybdenum and vanadium are both reduced by adding excess titanous chloride. Potassium thiocyanate indicator is then added, and the titration is completed with ferric chloride as usual.

Experimental

The balance used in this research was a chainomatic, easily sensitive to 0.1 mg. The weights used were calibrated by double weighings against a Bureau of Standards set, and by the method of Richards[72]. The single-deflection method of weighing was used almost exclusively[73]. All pipettes and burettes were calibrated by the weight of water delivered.

In most cases ordinary c. p. reagents, and distilled water were used, although in certain cases especially purified materials were prepared. For instance, iodine was resublimed to use as a primary standard for thiosulphate determinations, and Bureau of Standards sodium oxalate was used in standardizing permanganate solutions.

Most of the work done in this research was with solutions of vanadium and molybdenum which were purified and standardized as follows:

Preparation and Standardization of the Pure Molybdenum Solution

A high grade of "C. P." ammonium molybdate was twice recrystallized from hot water containing a small amount of ammonium hydroxide. The product was dissolved in distilled water containing a few drops of ammonia.

This solution remained perfectly clear for over a year. It was examined 15 months later, and found to contain a very slight precipitate, apparently due to the action of the ammonia on the glass bottle.

The solution was standardized gravimetrically as $PbMoO_4$. Definite volumes of the solution were taken with a 25 c. c. pipette, diluted to about 200 c. c., and a slight excess of acetic acid and 5 or 10 g. of ammonium acetate were added. A slight excess of 4% lead acetate reagent was then added, and the mixture was heated to boiling. It was kept hot for about 15 minutes, and allowed to stand until the precipitate had settled. The precipitate was then filtered on paper, washed with hot 2% ammonium nitrate solution, ignited wet in a porcelain crucible, and weighed.

Volume solution taken	Weight of $PbMoO_4$	MoO_3 found
25 c. c.	0.5083 g.	0.1994 g.
25	0.5113	0.2006
25	0.5084	0.1994
25	0.5092	0.1997
25	0.5132	0.2014
25	0.5105	0.2003
25	0.5109	0.2004
25	0.5126	0.2011
		Average 0.2004

The solution was also standardized by the zinc reductor method. 25 c. c. of the solution were diluted to 100 c. c. and treated with 5 c. c. of concentrated sulphuric

[72] J. Am. Chem. Soc. 22, 144 (1900).
[73] Paul H. M.-P. Brinton, J. Am. Chem. Soc. 41, 1151 (1919).

acid. After warming to about 50° C., the solution was passed through a column of zinc, and caught in a solution of ferric alum. The purpose of this was to prevent the reduced molybdenum from being reoxidized by the air before titration. The reductor was rinsed out with warm 2.5% sulphuric acid, and the resulting reduced molybdenum solution was titrated with 0.1023 N. permanganate. A blank on the reductor amounted to 0.25 c. c. which was subtracted from the titration volume.

Volume solution taken	$KmnO_4$—blank used	MoO_3 found
25 c. c.	40.82 c. c.	0.2004 g.
25	40.88	0.2007
25	40.83	0.2004
		Average 0.2005

Summary of Standardization

By the $PbMoO_4$ method, 25 c. c. contain 0.2004 ± 0.0010 g.

By the zinc reduction method, 25 c. c. contain 0.2005 ± 0.0002 g.

Preparation and Standardization of the Pure Vanadium Solution

The starting materials for the preparation of pure vanadium solutions were ammonium vanadate or vanadium pentoxide. If the oxide was used, it was treated with ammonium hydroxide and heated until nothing more would dissolve. The insoluble matter was filtered off. If ammonium vanadate was the beginning material, it was dissolved in water containing a little ammonia, and any insoluble matter filtered off. In either case, the resulting solution upon cooling, deposited crystals of ammonium vanadate, which were filtered with suction, and washed with cold water. The material was redissolved in boiling slightly ammoniacal water, and recrystallized. It was found that rapid cooling of the hot solution with stirring caused the ammonium vanadate to separate in small fluffy flakes, which did not adhere to the walls of the containing vessel, as was the case when the solution was allowed to cool slowly. Under the latter conditions, the ammonium vanadate deposited on the sides of the beaker, and caked so much that it was difficult to remove it. The ammonium salt was then converted into the pentoxide, V_2O_5, by calcining it in a porcelain dish at about 400° C. Most of the product obtained by this treatment was orange colored, but there was also present a small quantity of a black lower oxide, which had apparently been reduced by the ammonia. The residue was moistened with pure nitric acid, and again heated to 400° in a muffle. The material was now a uniform yellowish-orange powder.

The first solution was prepared by suspending some of the above oxide in water in a platinum dish, and passing ammonia gas until, upon warming, complete solution was obtained. The hot solution was filtered, and allowed to crystallize in a platinum dish. The crystals were filtered off with the aid of suction, and dried between filter paper. This material was pure white in color.

A standard vanadium solution was prepared by dissolving this purified product in water. Owing to the small solubility of the ammonium salt in water, some concentrated hydrochloric acid was added to increase the solubility. Considerable hydrochloric acid was required to get the desired amount of ammonium vanadate into solution. This had the serious disadvantage of reducing some of the vanadium to the tetravalent condition. Consequently, the next vanadium solution was made by adding pure V_2O_5 in small quantities at a time to a hot concentrated solution of sodium bicarbonate. The V_2O_5 dissolved rapidly and completely, liberating a corresponding amount of carbon dioxide. The sodium vanadate solution thus pre-

pared was very permanent. A six months old solution was examined and found to be just as clear as the day it was prepared.

The first vanadium solution was standardized by several methods.

By direct evaporation of 25 c. c. portions in large porcelain crucibles, followed by ignition in a muffle at 400-500° C., the following values were obtained.

Volume solution taken	V_2O_5 found
25 c. c.	0.1536 g.
25	0.1535
25	0.1535
	Average 0.1535

By precipitating from neutral solution with mercurous nitrate solution, and igniting to V_2O_5.

25	0.1543
25	0.1513
25	0.1553
	Average 0.1536

By the zinc reductor method, catching the reduced solution in ferric alum, and titrating with 0.1023N. permanganate. The "blank" on the reductor amounted to 0.2 c. c. of permanganate.

Volume solution taken	$KMnO_4$—blank used	V_2O_5 found
25 c. c.	48.95 c. c.	0.1519 g.
25	49.11	0.1524
25	49.30	0.1530
25	49.25	0.1528
		Average 0.1525

By reducing the solution by triple evaporation to sulphur trioxide fumes, with intermittent additions of 20 c. c. of concentrated hydrochloric acid, finally diluting to 200 c. c. and titrating with 0.1023 N. permanganate. The titration was made at 70° C.

Volume solution taken	$KMnO_4$ required	V_2O_5
25 c. c.	16.48 c. c.	0.1534
25	16.51	0.1537
25	16.36	0.1523
		Average 0.1531

Summary of Standardization of the First Solution

By direct evaporation	0.1535 ± 0.0001 g. V_2O_5
With mercurous nitrate.	0.1536 ± 0.0023
By zinc reduction.	0.1525 ± 0.0005
By hydrochloric acid reduction.	0.1531 ± 0.0008

All of these results are calculated from a basis of 25 c. c. of the standard solution.

Standardization of the Second Vanadium Solution

A second solution, prepared by dissolving V_2O_5 in a hot solution of sodium bicarbonate, was standardized by the zinc reductor method as above. The permanganate used was 0.1023 N. The "blank" of 0.38 c. c. was subtracted from the total.

Solution taken	$KMnO_4$—blank used	V_2O_5 found	V_2O_5/10 c. c.
10 c. c.	31.62 c. c.	0.0981 g.	0.0981 g.
10	31.59	0.0980	0.0980
20	63.33	0.1965	0.0983
20	63.19	0.1961	0.0981
			Average 0.0981

By Holverscheit's method; i. e., distilling with 2 or 3 grams of potassium bromide and 30 c. c. of concentrated hydrochloric acid, and catching the liberated bromine in potassium iodide solution. The liberated iodine was then titrated with thiosulphate solution which had been standardized against pure resublimed iodine, and against 0.1023 N. permanganate. The thiosulphate was found to be 0.04574 N.

Volume taken	$Na_2S_2O_3$ required	V_2O_5 found	V_2O_5/10 c. c.
10 c. c.	23.63 c. c.	0.0984 g.	0.0984 g.
10	23.60	0.0982	0.0982
10	23.63	0.0984	0.0984
10	23.58	0.0981	0.0981
10	23.69	0.0986	0.0986
10	23.56	0.0981	0.0981
20	47.00	0.1956	0.0978
20	47.02	0.1957	0.0979
30	70.34	0.2928	0.0976
			Average 0.0981

By Muller and Diefenthaler's[42] method, which was carried out as follows: The neutral vanadate solution was diluted to 70 c. c. 2.5 g. of solid potassium ferrocyanide were added, and stirred until dissolved, after which 20 c. c. of 2N. sulphuric acid were added. Under this treatment, the vanadium is reduced to a vanadyl compound, and a corresponding amount of potassium ferricyanide is formed. 3 g. of potassium iodide were then added, and the solution stirred until dissolved. Then 20 c. c. of a solution of zinc sulphate (150 g. per liter) were added, and after a few minutes standing, the solution was diluted to 200 c. c. and the iodine liberated was titrated with thiosulphate, using starch as an indicator. The thiosulphate was 0.0474 N.

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	22.82 c. c.	0.0984 g.
10	22.81	0.0984
10	22.80	0.0983
10	22.74	0.0981
		Average 0.0983

One determination by this method in the presence of 0.08 g. of MoO_3 was attempted, but although it is probable that the molybdenum is not reduced, and does not interfere in this way, the color of the resulting reddish-brown molybdenum ferrocyanide is so intense that the detection of the end point is very difficult, if not impossible.

Summary of Standardization of the Second Solution

The results are expressed in the number of grams of V_2O_5 per 10 c. c. of the solution.

By zinc reduction.	0.0981 ± 0.0002 g.
By Holverscheit's method.	0.0981 ± 0.0005
By Muller and Diefenthaler's method.	0.0983 ± 0.0002

The following are the most important points that were investigated in this research:

I. The temperature at which pure molybdenum trioxide begins to volatilize was accurately determined.

II. Some work was done on the conversion of molybdenum sulphide to the oxide.

III. A study was made of the separation of molybdenum from vanadium as sulphide.

IV. An iodometric method for the determination of vanadium was developed.

V. Several methods for the separation of vanadium and molybdenum were found to be unsatisfactory.

The Determination of the Volatilization Point of Molybdenum Trioxide

The temperature to which molybdenum trisulphide can be heated in its conversion to the oxide as a weighing form for molybdenum has long been a matter of dispute. It is well known that molybdenum trioxide begins to sublime at a temperature below its melting point. The exact temperature, however, has apparently not been definitely established.

According to Treadwell[74], ammonium molybdate can be changed to the oxide by igniting in a spaceous crucible; at first gently, and later at a dull red heat. He says there is no danger of losing any molybdenum by volatilization, providing the dull red heat is not exceeded.

Wolf[75] states that the conversion of a precipitate of molybdenum sulphide into molybdenum trioxide by ignition is not quantitative if the temperature rises above 450°, as sublimation then occurs to an appreciable extent. A temperature of 400° suffices, and it is most convenient and certain to ignite the precipitate in an electrically heated furnace at a temperature of 425° C.

Johnson[76] ignites in a large porcelain crucible at 500° to 550° C.

Scott[77] states that the oxide (MoO_3) sublimes at a bright red heat. Groschuff[78] says the melting point of molybdenum trioxide is 791° C. in the absence of reducing agents, at which point it melts undecomposed. He further states that the anhydride begins to sublime in the neighborhood of the melting point.

The following statement occurs in Bulletin 212, Bureau of Mines[79], "MoO_3 can be completely volatilized at temperatures around 700° C., although this volatilization begins at around 500° C." Other authors use terms such as, "Ignite at a low temperature," "Heat with a low flame," etc.

[74] Treadwell and Hall, Analytical Chemistry. Vol. II. 5th ed., John Wiley and Sons, New York (1919), p. 284.
[75] Z. angew. Chem. (1) 31, 140 (1918).
[76] Opus cit., p. 157.
[77] Standard Methods of Chemical Analysis, 1920, p. 279, D. Van Nostrand Co.
[78] Z. anorg. Chem. 58, 113 (1908).
[79] Opus cit., p. 83.

The need for accurate data on the volatilization point thus becomes apparent.

The first step in this determination was the preparation of the pure oxide, MoO_3. The starting point was a high grade of "C. P." ammonium molybdate. This was recrystallized once from redistilled water. After filtering off the crystals and washing them with cold water, they were redissolved in the minimum amount of redistilled water, and the solution was placed in a porcelain dish. Pure concentrated nitric acid[1] was then added in slight excess of the amount required to precipitate molybdic acid. The solution was then boiled for about half an hour to decompose the ammonium salt. The solution was cooled, the molybdic acid filtered off, and washed with cold water. It was dried at 110°C.

The material was then further purified by sublimation. The apparatus used was a platinum dish tightly fitted in a hole in a piece of asbestos board, the top of the dish extending about one-half an inch above the surface of the board. The platinum dish was covered with an inverted quartz dish which rested on the surface of the asbestos board. The material to be sublimed was placed in the platinum dish and heated to fusion over a blast lamp. The light fluffy sublimate gathered on the sides of the dish, and was removed from time to time.

The product was tinged slightly greenish, and was very hard to handle because of its light fluffy nature. It was suspended in water, and ammonia gas was passed into it. Everything but a trace went into solution on warming.

The ammonium molybdate solution thus formed was treated as before with pure nitric acid, which again precipitated molybdic acid. After boiling about half an hour, the solution was cooled, the molybdic acid filtered off, washed with cold water, and dried at 110° C.

A preliminary test of this material showed that it still contained volatile matter, either water or ammonium salts, or both; since a weighed sample lost over 2% of its weight on heating to 160° C. A small portion when heated in a porcelain crucible to faint redness, suddenly turned grayish green. This together with a Nessler's test on the material, indicated the presence of appreciable amounts of ammonium salts.

The material was then taken up in water and boiled with more pure nitric acid. The liquid was decanted from time to time and discarded, being replaced by more fresh water and nitric acid. Even after several treatments by this method, a small portion of the material still darkened on heating in a porcelain crucible.

Therefore the whole material was placed in a quartz dish and heated to redness with a Bunsen flame. The powder was stirred during the heating until a uniform looking grayish mass resulted. After cooling, it was treated with enough nitric acid to make it pasty, and heated to 200°-300° in a muffle. It was cooled, treated with more nitric acid, and again heated in a muffle to 200°-300° C.

The material was ground in an agate mortar, and preserved in a stoppered weighing bottle. In appearance, it was a heavy powder, slightly yellowish green in color, indicating a possible trace of reduction. On heating to 400° C. for an hour or two the greenish color disappeared.

The volatilization point of this pure molybdenum trioxide was determined by heating it for long periods of time at definite temperatures, and noting the losses

[1] The nitric acid was purified by redistilling the C. P. reagent in an all glass retort. 10 c. c. of the acid, when evaporated to dryness and ignited in a platinum crucible, gave a residue weighing 0.0002 g.

in weight. An 8-inch tubular electric furnace with rheostat temperature control was used. A 16 in. x 1 in. transparent fused silica tube was inserted in the furnace in such a way that equal portions of the tube protruded from each end of the furnace. The molybdenum trioxide was placed in a boat at the exact center of the tube. The temperature was measured by means of a base metal thermocouple*, the hot junction of which was placed within the quartz tube even with the middle of the boat. It was found that the temperature could be kept constant to ± 10° C. for long periods of time. Part of the time, a slow current of air, purified by bubbling through concentrated sulphuric acid, and then through a U tube filled with soda-lime, was passed through the tube.

Trial No. I.—MoO_3 taken 0.5913 g.

Time at a given temp.	Temp. ± 5° C.	Loss in weight
4 hr.	375°-400°	0.0001 g
10	400	0.0000
3	430	0.0000
3	450	0.0000
6	470	0.0000
9	490	0.0000
5	505	0.0001
3	535	0.0000
3	520	0.0001
3	525-565	0.0001
2	585	0.0002
10	580	0.0002
2.5	610-620	0.0007
5	610	0.0015
3	640	0.0011
11	640	0.0049
0.5 (30 min.)	745	0.0295

Trial No. II.—MoO_3 taken 0.9489 g.

Time at a given temp.	Temp. ± 5° C.	Loss in weight
3 hr.	535°	Gained 0.0002 g.
15	550	0.0002
11	495	0.0000
8	505	0.0001
12	550	0.0003
12	560	0.0001
5	590	0.0005
11	645	0.0046

Trial No. III.—MoO_3 taken 0.4991 g.

4 hr.	500°	0.0000 g.
5	525	0.0001
12	490-525	0.0000
5	495	0.0000
11	555	0.0002
3	600	0.0000
14	570-590	0.0004
4	650	0.0014

In all three cases, the first definitely visible sublimate deposited on the transparent silica tube did not appear until the 600° C. mark had been passed.

After these trials the thermocouple was checked with a standard 400° thermom-

* The thermocouple had previously been calibrated by direct comparison with a standard Hoskins couple, which had been calibrated by the Bureau of Standards.

eter (by direct comparison). The thermocouple was found to read low by not over 5° C. at a temperature of around 400° C.

These experiments show that there is absolutely no loss of molybdenum trioxide below 500° C. Between 500° and 600° C. there is a slight loss, but not sufficient to make the temperature dangerous for igniting molybdenum trioxide for ordinary periods of time. For instance, the loss in this interval was never greater than 0.0001 g. per hour, and was usually much less. Above 600° C. however, the loss becomes appreciable; in the interval between 600°-650° C., the loss is about 0.0004 g. per hour. Therefore temperatures above 600° C. are not suitable for accurate analytical work, and in igniting precipitaties of molybdenum sulphide, this temperature should not be exceeded.

The Conversion of Molybdenum Sulphide to the Trioxide

The problem of completely converting molybdenum trisulphide into molybdenum trioxide as a weighing form for molybdenum has long been recognized as a troublesome procedure. If too low a temperature is used, the oxidation may not be complete, while if the temperature is too high, there is danger of volatilizing some of the molybdenum trioxide resulting from the ignition.

Treadwell[80] gives two methods of procedure. If the precipitate of molybdenum sulphide has been filtered on paper the moist filter is placed in a large porcelain crucible, and dried on the water bath. The crucible is then covered, and very carefully heated with a small flame until no more hydrocarbons are expelled. The cover is then removed, the carbon burned from the sides of the crucible at as low a temperature as possible, and, by raising the temperature gradually, the sulphide is changed to oxide. The operation is finished when no more sulphur dioxide is formed. After cooling, a little mercuric oxide (suspended in water) is added to the contents of the crucible, the mixture is well stirred, evaporated to dryness on the water bath, the mercuric oxide is removed by gentle ignition, and the residue of molybdenum trioxide is weighed.

An easier way to transform the sulphide into oxide is to filter the precipitate on a Gooch crucible, wash first with water containing a little sulphuric acid, and then with alcohol, and dry at 100° C. The crucible is then placed in a larger nickel one, covered with a watch glass, and carefully heated over a small flame whereby the sulphide is for the most part changed to oxide. As soon as the odor of sulphur dioxide can no longer be detected, the watch glass is removed, and the open crucible heated until it is brought to constant weight. The molybdenum oxide thus obtained always contains traces of sulphate, and consequently has a bluish appearance. The results nevertheless are said to be excellent.

Taggart and Smith[81] dry the precipitate of molybdenum sulphide, mix it with anhydrous oxalic acid, and claim that by careful ignition conversion to the trioxide takes place quite easily.

Hundeshagen[82] adds nitric acid to the precipitate and evaporates to low volume; then ignites to the oxide. Seligssohn[83] ignites with lead oxide and ammonium nitrate. Binder says, "When molybdenum is precipitated as MoS_3 and then ignited to oxide, the oxidation is not complete unless the substance, after preliminary

[80] Opus cit., p. 286.
[81] J. Am. Chem. Soc. 18, 1054 (1896).
[82] Z. anal. Chem. 28, 142 (1889).
[83] J. prakt. Chem. (1) 67, 472 (1856).

ignition, is treated with nitric acid, evaporated, dissolved in ammonia, reprecipitated with nitric acid, evaporated, and ignited. A correction must be made for any traces of matter which remain insoluble when the ignited residue is dissolved in ammonia[84]."

Johnson[85] ignites the precipitated sulphide in a spacious porcelain crucible at 500° to 550° C. The residue is extracted with ammonia, and the insoluble matter is filtered, ignited and weighed. The difference in the two weights is the amount of molybdenum oxide present.

Experimental

A few experiments were made on the completeness of the conversion of molybdenum sulphide to oxide by ignition in the air. To obtain data upon which to work, a crude muffle was made from a large (50 c. c.) porcelain crucible. A piece of asbestos board just large enough to cover the bottom of the crucible was cut out, and placed in the crucible. A support for the crucible containing the precipitate was made from a nichrome triangle bent to fit inside of the outer crucible, and supported by bending the wires of the triangle ends over the rim of the outer crucible.

Some pure molybdenum oxide was first heated in the muffle to determine whether or not the temperature was too high. About 0.4 g. of the material was weighed out in a porcelain crucible, placed in the muffle, and heated with the flame of a Tirril burner. The bottom of the muffle was about 2.5 inches above the top of the burner. Igniting for one hour periods with the full heat of the Tirril burner gave a loss in weight of 0.0006 g. With a more moderate flame, one about 5 inches high, the maximum loss after one hour of heating was not over 0.0001 g. This, then, was about the limit of temperature that could be used for the ignition. The absence of the asbestos board in this muffle would also give too high a temperature, and cause loss by sublimation.

Measured portions of a standard ammonium molybdate solution were pipetted into beakers, diluted to 150 c. c., and treated with 5 c. c. of 6N. ammonium hydroxide. The solution was saturated with hydrogen sulphide, and allowed to stand until the red thiomolybdate formed. It was found that the red coloration developed much faster in a warm solution than in a cold one. The cold solution was then slightly acidified with strong sulphuric acid, and warmed a few minutes to coagulate the precipitate which separated at this point. After allowing the precipitate to settle, it was filtered on paper, and washed with warm water containing hydrogen sulphide.

The wet precipitate and paper were ignited in the muffle furnace described above. A flame from a Tirril burner about 5 inches high was used.

In the following table are shown the results of determinations on separate portions of the standard ammonium molybdate solution.

[84] Chem. Ztg. 42, 255 (1918).
[85] Opus cit., p. 157.

MoO_3 taken	MoO_3 found	Difference
0.0799 g.	0.0799 g.	0.0000 g.
0.0799	0.0802	+0.0003
0.0799	0.0798	—0.0001
0.0799	0.0799	0.0000
0.0799	0.0800	+0.0001
0.0799	0.0800	+0.0001
0.0799	0.0810	+0.0011
0.0799	0.0794	—0.0005
0.0799	0.0799	0.0000
0.0799	0.0804	+0.0005
0.0799	0.0797	—0.0002
0.1598	0.1594	—0.0004
0.1598	0.1598	0.0000
0.1598	0.1601	+0.0003
0.1598	0.1597	—0.0001
0.1598	0.1600	+0.0002
0.2397	0.2393	—0.0004
0.2397	0.2390	—0.0007

Several of the filtrates were evaporated to dryness with nitric acid, taken up in ammonium hydroxide and water, again saturated with hydrogen sulphide, and acidified with sulphuric acid. In no case did more than a trace of precipitate settle out on standing, and in some cases there was no precipitate at all. In one case the precipitate was filtered, ignited in the air muffle, and weighed. The weight was found to be 0.0002 g.

All of the above precipitates came to constant weight within one hour's ignition for quantities of molybdenum trioxide less than 0.1 g. For larger amounts, two hours were in some cases necessary. The ignited residues usually had a slightly grayish cast. After the filters were once placed in the muffle they required no further attention until they were ready to be cooled and weighed.

It is thus shown that molybdenum sulphide can be satisfactorily ignited to molybdenum trioxide in the air.

The Separation of Molybdenum from Vanadium as Sulphide

It has been shown that molybdenum can be separated from vanadium by precipitating it as sulphide with hydrogen sulphide in slightly acid solution. The vanadium remains entirely in solution under this treatment. To secure complete precipitation of the molybdenum however, it is necessary to use increased pressure, as has been shown by a number of investigators. Friedheim and Euler[86] have demonstrated the accuracy of this method. They obtained the best results by first reducing the vanadium to the vanadyl condition with sulphur dioxide. Cruser and Miller[87] also found a complete separation of smaller quantities of molybdenum from vanadium and iron, using hydrogen sulphide in acid solution with pressure.

Johnson[88] saturates the neutral solution containing tartrate with hydrogen sulphide. Under these conditions a soluble red thiomolybdate forms. The solution is then treated with sufficient strong hydrochloric or sulphuric acid to completely coagulate the precipitate of molybdenum sulphide, meanwhile continuing the passage of hydrogen sulphide into the solution. After filtering and washing, the precipitate is ignited in a spacious porcelain crucible to the oxide, and weighed.

[86] Loc. cit.
[87] J. Am. Chem. Soc. 26, 675 (1904).
[88] Opus cit., p. 167.

The residue is dissolved in ammonium hydroxide, and any insoluble matter is filtered off and again ignited. The difference between the two weights gives the amount of molybdenum trioxide present. He gives data showing the recovery of 0.2000, 0.1990, and 0.1995 g. of MoO_3 from mixtures of 0.1995 g. of MoO_3 with 0.050, 0.150, and 0.100 g. of V_2O_5 respectively. He further states that some of the vanadium was found in the filtrate when the molybdenum sulphide was filtered off, and part of it in the residue from the ammonia extraction of the ignited precipitate. 5 g. of tartaric acid were used in each case, and the precipitation was made as stated above.

Low[89] saturates the ammoniacal solution with hydrogen sulphide in the presence of tartrate. Upon acidifying the resulting solution, the molybdenum is precipitated as sulphide. The object of this method is to do away with the necessity of using increased pressure. The tartaric acid is added for the purpose of preventing the precipitation of vanadium when the solution is acidified. A similar method has been developed by the Electro Metallurgical Co. in co-operation with Ledoux and Co., as described in Bureau of Mines Bulletin 212[90].

Experimental

A number of determinations were made by both methods; i. e., precipitation with hydrogen sulphide in acid solution using pressure; and acidification of the ammonium sulphide solution of the thiomolybdate and thiovanadate containing ammonium tartrate.

The Separation of Molybdenum from Vanadium in Acid Solution with Hydrogen Sulphide

A series of determinations on a standard solution of ammonium molybdate were first made as follows. The solution was diluted to 100 c. c., and acidified with 5 c. c. of dilute sulphuric acid. It was placed in a pressure bottle and saturated with hydrogen sulphide gas. The flask was closed and heated to the boiling point on the water bath. After allowing the solution to cool to room temperature, the precipitate was filtered, and washed with warm hydrogen sulphide water containing a few drops of sulphuric acid. The precipitate was ignited in the air muffle (see page 20) to constant weight. The filtrates were boiled down to about 50 c. c. and treated with a little bromine water. After expelling the excess bromine by boiling, a second pressure precipitation was made. In all cases, although no precipitate was visible in the solution, a small amount collected when the solution was filtered.

The following results were obtained.

MoO_3 taken	MoO_3 found 1st ppt.	MoO_3 found 2nd ppt.	MoO_3 found total
0.0799 g.	0.0797 g.	0.0002	0.0799 g.
0.0799	0.0793	0.0003	0.0796
0.0799	0.0799	0.0002	0.0801
0.0799	0.0795	0.0001	0.0796
0.0799	0.0793	0.0002	0.0795
0.0799	0.0794	0.0003	0.0797
0.0799	0.0797	0.0003	0.0800
0.0799	0.0800	0.0006	0.0806

To determine the effect of vanadium under these conditions, two determinations containing vanadium only were made as above.

[89] Opus cit., p. 163.
[90] Opus cit., p. 121.

V_2O_5	Weight of precipitate
0.1630 g.	0.0002 g.
0.1788	0.0002

Allowing 0.1 mg. for the ash of the filter paper, this gives a residue of vanadium pentoxide of only 0.0001 g.

Mixtures of molybdenum and vanadium were then treated as above. The filtrates in most cases were treated with nitric acid and evaporated to fumes of sulphur trioxide, diluted to about 100 c. c., and the pressure precipitation was repeated.

The following results were obtained:

MoO_3 taken	V_2O_5 taken	MoO_3 found 1st ppt.	MoO_3 found 2nd ppt.	V_2O_5 in 1st ppt.
0.0799 g.	0.0186 g.	0.0796 g.	0.0003 g.	0.0000 g.
0.0799	0.0448	0.0797	not det.	not det.
0.0799	0.0451	0.0797	0.0001	0.0001
0.0799	0.0537	0.0798	not det.	not det.
0.0799	0.0867	0.0801	0.0006	0.0003
0.0799	0.1267	0.0799	0.0004	0.0003
0.0799	0.1391	0.0808	not det.	not det.
0.0799	0.3293	0.0805	0.0004	not det.
0.2397	0.1567	0.2395	0.0010	0.0004
0.2397	0.2236	0.2388	0.0013	0.0004

The small amount of precipitate that was recovered from the filtrate from the first precipitation was found to consist of both molybdenum and vanadium.

The ignited residue from the main precipitate was in some cases dissolved in a small amount of ammonium hydroxide, and tested for vanadium by adding a solution of diphenyl-amine and hydrochloric acid. This test is due to Maurio[5], and is performed as follows: The solution was transferred to a 50 c. c. Nessler jar, diluted to 40 c. c., and 5 c. c. of concentrated hydrochloric acid and 5 c. c. of diphenyl-amine reagent were added. (The diphenyl-amine reagent is prepared by warming 0.2 g. of the solid with 100 c. c. of water for some time on the water bath, and filtering the cool solution.) In the presence of vanadium a violet coloration gradually appears.

When the test was applied to one of the pure molybdenum trioxide precipitates that had been obtained from a pure molybdenum solution containing no added vanadium, no violet coloration appeared even after standing for one hour. At the end of this time the solution had a greenish tinge, but no violet. When 0.2 mg. of vanadium pentoxide was added to this solution however, a violet coloration appeared after standing about 2 minutes, and reached its maximum intensity after about 10 minutes. It was found possible to estimate by this test, the approximate amount of vanadium present up to about 0.5 mg. In the presence of larger quantities of vanadium the coloration produced is so intense, that even an approximate estimate of the amount present is not possible.

All of the precipitates from the molybdenum-vanadium mixtures that were examined gave a positive test for vanadium. In no case was more than 0.3 or 0.4 mg. of V_2O_5 present however, and usually a smaller amount was found.

Some additional separations were made just like the above with the addition of 2 grams of tartaric acid. It was thought possible that the tartaric acid might help keep the vanadium in solution.

The following results were obtained.

MoO_3 taken	V_2O_5 taken	MoO_3 found 1st ppt.	MoO_3 found 2nd ppt.	V_2O_5 found in 1st ppt.
0.0799 g.	0.0571	0.0798 g.	0.0005 g.	0.1 mg.
0.0799	0.0700	0.0799	not det.	0.4
0.0799	0.0738	0.0800	0.0002	0.3
0.0799	0.1178	0.0803	0.0005	0.4
0.0799	0.1231	0.0806	not det.	0.4
0.0799	0.1431	0.0801	0.0001	0.3

The filtrates in each case were evaporated with nitric acid to fumes of sulphur trioxide. After the organic matter had been completely destroyed by repeated evaporations with nitric acid, the solutions were diluted to 100 c. c., 2 grams more of tartaric acid were added, and the pressure precipitations were repeated.

The residues from the main precipitates were dissolved in ammonia, and tested for vanadium with the diphenyl-amine reagent. In every case a strong test for vanadium was obtained.

The results indicate that tartaric acid has no function in preventing the precipitation of traces of vanadium with the molybdenum, since equally good results were obtained in the absence of tartaric acid.

A series of determinations in which the sulphuric acid was replaced by hydrochloric acid gave the following results. No tartaric acid was used in these determinations, and the filtrates were not examined for molybdenum.

MoO_3 taken	V_2O_5 taken	MoO_3 found
0.0799 g.	0.0000 g.	0.0795 g.
0.0799	0.0000	0.0789
0.0799	0.0378	0.0803
0.0799	0.0475	0.0805
0.0799	0.0776	0.0805
0.0799	0.1079	0.0795
0.0799	0.1162	0.0789
0.0799	0.1353	0.0787

As stated above, the filtrates from these determinations were not examined for molybdenum, although there was undoubtedly appreciable amounts of it present in some cases. The ignited precipitates were also not examined for the presence of vanadium. The results tend to indicate however, that hydrochloric acid is not as satisfactory as sulphuric acid in this determination.

The Separation of Molybdenum from Vanadium as Sulphide by Acidifying the Ammonium Sulphide Solution of Their Thio Salts in the Presence of Tartrates

Some determinations corresponding closely to the procedure given in Low[89] were made as follows. Measured quantities of standard molybdenum and vanadium solutions were mixed and diluted to about 200 c. c. 15 c. c. of 6N. ammonium

hydroxide were added, followed by 2 grams of solid tartaric acid. When the tartaric acid had dissolved, the solutions were saturated with hydrogen sulphide gas.*

They were then acidified with hydrochloric acid, and warmed to coagulate the precipitated molybdenum sulphide. The precipitate was filtered on paper, washed with warm water saturated with hydrogen sulphide, ignited in the air muffle as described above, and weighed. The following results were obtained:

MoO_3 taken	V_2O_5 taken	MoO_3 found	Difference
0.0799 g.	0.0856 g.	0.0816 g.	+0.0017 g.
0.0799	0.0856	0.0814	+0.0015
0.1598	0.0856	0.1609	+0.0011
0.1598	0.0856	0.1606	+0.0008
0.2397	0.0856	0.2418	+0.0021
0.2397	0.0856	0.2413	+0.0016

The filtrates were treated with nitric acid and evaporated to dryness on the steam bath. They were taken up in a little nitric acid and again evaporated to dryness. The residue was taken up in 10 c. c. of 6N. ammonium hydroxide, and 2 grams of tartaric acid were added. About 5 c. c. of saturated ammonium sulphide were added, and the solution was acidified with hydrochloric acid. In every case a milky precipitate appeared. This was allowed to digest in a warm place for several hours, after which a small light brown precipitate had settled. This was filtered off, washed, ignited, and weighed as above. The following results were obtained on the second precipitates.

Determination number	Weight of precipitate
1.	0.0013 g.
2.	0.0014
3.	0.0009
4.	0.0014
5.	0.0015
6.	0.0013

These precipitates were not almost white as one would expect a molybdenum trioxide residue to look, but were on the contrary dark brown in color. After constant weight had been obtained in the air muffle, they were ignited to fusion over the free flame of a Tirril burner. This did not change their weight. Upon testing the precipitates with hydrochloric acid and hydrogen peroxide, they were found to consist of pure vanadium pentoxide, and contained no molybdenum at all.

It would appear from this that the high results obtained from the first precipitation were due to vanadium coming down with the molybdenum sulphide,

* It has been the experience of Dr. P. H. M.-P. Brinton that a precipitate of molybdenum sulphide sometimes separates at this point, especially on long passage of hydrogen sulphide. He worked, however, in the absence of tartaric acid. He further states that this precipitate has the appearance of red selenium, and that it seems to do no harm at all, as remaining molybdenum is precipitated on the addition of hydrochloric acid.

This is contrary to my experience on pure solutions of ammonium molybdate. Solutions of 100 c. c. volume, containing 0.16 g. of molybdenum trioxide, and varying amounts of 6N. ammonium hydroxide from 1 to 20 c. c., when saturated with hydrogen sulphide gas, gave no immediate precipitate, nor was any visible after 24 hours standing.

In similar experiments on vanadium solutions however, a small precipitate was invariably obtained, especially with large quantities of vanadium. For instance, a solution of 0.23 g. of vanadium pentoxide in sodium bicarbonate, when treated with 1 c. c. of 6N. ammonia, and saturated with hydrogen sulphide, gave at once a considerable quantity of dark brown precipitate. A similar determination using 20 c. c. of 6N. ammonia gave analogous results. With smaller quantities of vanadium (0.065 g. per 100 c. c. containing 10 c. c. 6N. ammonia) a precipitate was obtained only when hydrogen sulphide was passed for some time.

since if the weight of the second precipitate be subtracted from that of the first satisfactory results for the determination of molybdenum would be obtained. This assumes that as much vanadium was carried down with the first precipitate as the second.

Other determinations in which the quantity of vanadium present was varied gave these results.

MoO_3 taken	V_2O_5	MoO_3 found 1st ppt.	MoO_3 found 2nd ppt.
0.0799 g.	0.0052 g.	0.0803 g.	0.0010 g.
0.0799	0.0078	0.0804	
0.0799	0.0175	0.0809	
0.0799	0.0209	0.0807	0.0011
0.0799	0.0372	0.0807	
0.0799	0.0412	0.0811	0.0011
0.0799	0.0500	0.0811	
0.0799	0.0526	0.0800	
0.0799	0.0661	0.0805	
0.0799	0.0688	0.0802	0.0010
0.0799	0.1989	0.0807	0.0014
0.0799	0.2494	0.0813	0.0011

The second precipitate in all cases consisted principally of vanadium pentoxide, with perhaps traces of molybdenum oxide.

Some of the precipitates were tested for vanadium with the diphenyl-amine test, and a strong positive test was usually obtained (over 0.5 mg. V_2O_5).

Three blanks on the reagents used, carried out just like the original determinations gave ignited residues weighing 0.0002, 0.0003, and 0.0002 g. respectively. 0.0001 g. of this is due to the ash in the filter paper used.

Another series of determinations like the above in the presence of vanadium only gave the following results. In all cases a heavy precipitate consisting mostly of sulphur, but containing appreciable quantities of vanadium, was obtained when the ammonium sulphide solution was acidified, and the solution was allowed to stand in a warm place for some hours to allow the precipitate to coagulate.

V_2O_5 taken	Weight of ignited precipitate
0.0088 g.	0.0006 g.
0.0183	0.0006
0.0358	0.0005
0.0839	0.0005

These determinations were made by passing hydrogen sulphide gas into the ammoniacal tartrate solutions. It was found that when ammonium sulphide was added directly, and the solution was acidified, more of the vanadium was precipitated. In the following determinations, the ammoniacal solution was treated with 2 grams of tartaric acid and 5 c. c. of concentrated ammonium sulphide, then acidified with sulphuric acid, filtered, washed, ignited, and weighed.

V_2O_5 taken	Weight of ignited precipitate
0.0202 g.	0.0008 g.
0.0369	0.0010

Warying the amount of tartaric acid present gave the following results.

V_2O_5 taken	Tartaric acid present	Weight of precipitate
0.065 g.	2 g.	0.0164 g.
0.065	5	0.0022
0.065	10	0.0013
0.013	2	0.0029
0.013	5	0.0032

In the above determinations, the precipitates containing only a small amount of vanadium were almost pure white or slightly yellowish in color (pure sulphur), while, as the vanadium content increased, the precipitates grew darker and darker in color.

Some additional determinations were made with the vanadium in the vanadyl state. Acid solutions of the vanadate were treated with 2 grams of tartaric acid, and boiled until they were pure blue in color, indicating complete reduction of the vanadium to the quadrivalent condition. The solutions were then diluted to 200 c. c., made ammoniacal, treated with 5 c. c. of ammonium sulphide reagent, and acidified with hydrochloric acid. When the precipitate had coagulated, it was filtered, washed, and ignited over a Bunsen flame.

V_2O_5 taken	Weight of precipitate
0.010 g.	0.0008 g.
0.010	0.0006
0.065	0.0016
0.065	0.0011

These results point to the conclusion that this method of separating molybdenum from vanadium cannot be very satisfactory in the presence of more than traces of vanadium. This conclusion is further borne out by the following determinations in which the molybdenum and vanadium were estimated volumetrically after being separated by the sulphide procedure.

Solutions containing known quantities of molybdenum and vanadium were mixed and diluted to 200 c. c. 5 c. c. of concentrated ammonium hydroxide and 2 grams of tartaric acid were added. The solutions were saturated with hydrogen sulphide, acidified with sulphuric acid, and warmed to about 50° C. to coagulate the precipitate. The precipitate was filtered and washed with 2% ammonium nitrate solution. 15 c. c. of concentrated nitric acid were added to the filtrate, and it was evaporated to fumes of sulphur trioxide to destroy the tartaric acid, and oxidize any molybdenum which may have escaped precipitation as sulphide. 5 c. c. more nitric acid were added and the mixture was again evaporated to fumes. The residue was taken up in water, made ammoniacal, and the ammonium sulphide process was repeated. The small brown precipitate obtained was filtered off and added to the main precipitate.

The precipitates and papers were placed in 250 c. c. beakers. 10 c. c. of concentrated nitric, and 6 c. c. of concentrated sulphuric acid were added, and the mixture evaporated to fumes of sulphur trioxide. More nitric acid was added, and the solution was again evaporated to fumes. This was repeated twice more to insure destruction of all the organic matter. The solution was finally fumed again after the addition of 5 c. c. of water, to remove the last traces of nitric acid. It was then diluted to 100 c. c., warmed slightly, and passed through a zinc reductor,

the lower end of which dipped below the surface of a ferric alum solution. After completely washing out the reductor with warm 5% sulphuric acid, the reduced solution was titrated with standard permanganate.

The filtrates, supposedly containing all of the vanadium, were evaporated to fumes of sulphur trioxide several times with nitric acid to oxidize the tartaric acid. They were then taken up in water, and passed through a zinc reductor similar to the molybdenum procedure above. A blank on the reductor was found to require 0.15 c. c. of permanganate.

The following results were obtained:

MoO_3 taken	MoO_3 found	V_2O_5 taken	V_2O_5 found
0.0816 g.	0.0823 g.	0.0000 g.	
0.1632	0.1620	0.0000	
0.0816	0.0830	0.0982	0.0972
0.1632	0.1648	0.0982	0.0969
0.1632	0.1645	0.0982	0.0972
0.2448	0.2450	0.0982	0.0971

These results, while not conclusive, confirm the others that this method of separation is not entirely satisfactory in the presence of appreciable amounts of vanadium.

It appears that a better separation of molybdenum from vanadium is obtained by passing hydrogen sulphide gas into the ammoniacal tartrate solution, and acidifying immediately, than when ammonium sulphide reagent is added directly. Long passage of the gas, or the addition of ammonium sulphide direct tends to increase the amount of vanadium precipitated. The amount of molybdenum present does not seem to affect the amount of vanadium which is precipitated. Likewise, the amount of vanadium present does not seem to have any relation to the amount which is precipitated. Just as much seems to come down from a solution containing 10 mg. of the pentoxide as from one containing 80 mg.

Summary

The most satisfactory method for the separation of molybdenum from vanadium as sulphide is precipitation with hydrogen sulphide in acid solution using pressure. Under these conditions not more than a few tenths of a milligram of vanadium pentoxide are ever carried down with the molybdenum, even when an abnormally large amount of vanadium is present.

The method of acidifying the ammonium sulphide solution of the thio salts in the presence of tartrates gives an unsatisfactory separation when appreciable amounts of vanadium are present. Vanadium is always found in the precipitate in amounts of 0.5 mg. or more.

The Iodometric Determination of Vanadium

From time to time several investigators have attempted to determine vanadium iodometrically in the same manner as we standardize thiosulphate solutions against any of our standard oxidizing agents, such as potassium dichromate, potassium permanganate, potassium iodate, etc. The method consists of adding a solution of potassium iodide to an acid solution of a vanadate, whereby the vanadium is reduced, liberating a corresponding amount of free iodine, which can be titrated with standard sodium thiosulphate solution using starch indicator.

The literature on the subject has been reviewed by Ditz and Bardach[91]. Holverscheit[10] found that when a solution of an alkali vanadate containing 0.1 g. of V_2O_5 was treated with potassium iodide and 50 c. c. of 1-1 sulphuric or a corresponding amount of hydrochloric acid, and the iodine liberated was titrated with standard thiosulphate solution, the results showed an over-reduction of V_2O_5 to V_2O_4 by 6.1 to 14.5%. He also found the end point hard to detect as it was difficult to distinguish between an iodine-starch blue and the blue of the vanadyl salt resulting from the reduction. Nevertheless, from the pure blue color of the resulting solution he thought it probable that the reduction went to the vanadyl state. Muller and Diefenthaler[42], upon addition of 3 grams of potassium iodide and molar sulphuric acid to the alkali vanadate, and titration of the resulting iodine with standard thiosulphate, found a reduction of over 11% above theoretical to the vanadyl compound. Wegelin[93] also noted an over-reduction.

By boiling a vanadate with potassium iodide and strong hydrochloric acid to a low volume in a Bunsen apparatus, Friedheim and Euler[30] noted an almost complete reduction to V_2O_3. According to the researches of Browning, when an ammonium vanadate solution is boiled with potassium iodide and sulphuric acid until all the iodine is expelled, the vanadium is in the tetravalent condition. Under the same conditions, Gooch and Curtis[92] boiled the solution in an atmosphere of carbon dioxide, collecting the iodine liberated in potassium iodide solution, and titrating with thiosulphate. They obtained results higher than those corresponding to reduction to vanadyl. By boiling the solution with concentrated hydrochloric acid down to 2 c. c. they obtained a quantitative reduction to V_2O_3.

Hett and Gilbert[95] treated an alkali vanadate solution with potassium iodide and hydrochloric or sulphuric acid at ordinary temperature, titrating the iodine liberated with thiosulphate. They obtained slightly high results, and concluded that while the method was perhaps not accurate enough for pure vanadium salts, it was satisfactory for ores, and similar products.

Warynski and Mdivani[94] reduced ammonium vanadate by distilling with potassium iodide and trichloracetic acid, and from the amount of iodine liberated concluded quantitative reduction to the vanadyl state. Ditz and Bardach[91] concluded, from their work at considerable dilution, that the reduction proceeded irregularly, and that the iodine liberated corresponds approximately to reduction to V_2O_3, or in some cases to an even lower oxide. Graham Edgar[95] repeated the work of Ditz and Bardach, and by avoiding atmospheric oxidation, showed that the reduction does not go beyond the vanadyl condition. He further concluded that V_2O_5 had a great effect in atmospheric oxidation of hydriodic acid, while V_2O_4 does not, and suggested that the high results obtained by Ditz and Bardach were due to this point.

Additional evidence that hydriodic acid reduces vanadates only to the tetravalent condition has been supplied by Perkins[17]. He found that when a slightly acid solution of a vanadate was shaken with a solution of potassium iodide and electrolytic silver, the free iodine liberated combines with the silver as silver iodide. The reduction goes only to the tetravalent condition.

[91] Z. anal. Chem. 53, 81 (1914).
[92] Am. J. Sci. (4) 17, 41 (1904).
[93] Z. offentl. Chem. 12, 265 (1906).
[94] Mon. Sci. 22, 527 (1908).
[95] J. Am. Chem. Soc. 38, 2369 (1916).

Experimental

When potassium iodide is added to a dilute acid solution of a vanadate, and the iodine liberated is titrated at once with standard sodium thiosulphate using starch indicator, an end point is reached before the theoretical reduction to V_2O_4. This end point is very fleeting however, and gradually returns. If the solution is again decolorized by the addition of more thiosulphate, the end point will still continue to come back.

The degree of reduction depends upon the dilution, the amount of acid and potassium iodide present, and the time of standing before titration. This is bourne out by the following experiments. Three solutions of ammonium vanadate, each containing 0.0650 g. V_2O_5, but diluted to different volumes, were treated with 5 c. c. of concentrated hydrochloric acid and 3 g. of potassium iodide. After standing one minute, the solutions were diluted to about 300 c. c. and titrated with 0.0507 N. thiosulphate. The first solution had an initial volume of 40 c. c., and required 14.23 c. c. of thiosulphate, equivalent to 0.0638 g. V_2O_5. The second had an initial volume of 70 c. c., and required 8.18 c. c. of the thiosulphate, equivalent to 0.0377 g. V_2O_5. The third had an initial volume of 90 c. c., and required 2.87 c. c. of the thiosulphate, equivalent to 0.0132 g. V_2O_5.

If the amount of acid and iodide are increased, high results are always obtained. This may be illustrated by the following experiment. A solution containing the same amount of vanadium as the above, was diluted to 200 c. c. 25 c. c. of concentrated hydrochloric acid and 5 grams of potassium iodide were added, and the solution was titrated immediately with 0.0507 N. thiosulphate. 17.70 c. c. were required, which corresponds to 0.0815 g. V_2O_5, or a result of 24.6% above theoretical.

If however, to a concentrated neutral solution of a vanadate (about 10 c. c. in volume) 5 or 10 c. c. of a mineral acid and a few grams of potassium iodide are added, iodine is immediately and quantitatively liberated according to the equation,

$$V_2O_5 + 2HI = V_2O_4 + I_2 + H_2O.$$

The iodine can be estimated very accurately by diluting the solution to 200 or 300 c. c., adding standard thiosulphate solution until most of the yellow color has disappeared, then adding starch, and finishing the titration to a pale blue. The end point corresponds very closely to that of the similar iodometric determination of a dichromate, in which the end point is found when one drop of thiosulphate changes the color of the solution from a blue to a sea green. In the case of vanadium however, the color change is from a dark blue to a pale blue. The end point is extremely sharp if good starch is used; it is so sharp in fact that a fraction of a drop of N/20 thiosulphate will give an unmistakeable end point. The end point is not extremely permanent, but depends somewhat on the amount of acid present. Ordinarily it will last at least 5 minutes.

Iodometric determinations of vanadium were made on two materials; a solution of sodium vanadate, and pure solid vanadium pentoxide.

Standardization of the Sodium Vanadate Solution

The solution was standardized by the zinc reductor method with the following results. The permanganate was standardized against sodium oxalate, and found

to be 0.0962 N. A blank on the reductor was found to be 0.2 c. c. The first series of determinations was made in November, 1923.

Volume solution taken	$KMnO_4$—blank	V_2O_5 found
10 c. c.	29.08 c. c.	0.0849 g.
10	29.06	0.0848
10	29.00	0.0846
10	29.04	0.0847
		Average 0.0848

The following series was made in March, 1924. Thee procedure was identical to the above:

10	29.39	0.0857
10	29.32	0.0855
10	29.30	0.0855
10	29.25	0.0854
10	29.30	0.0855
10	29.19	0.0852
		Average 0.0855

By Holverscheit's potassium bromide distillation method. The thiosulphate had been standardized against resublimed iodine and against standard permanganate, the two results agreeing within experimental error. The value taken was 0.04693 N.

Volume solution	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	19.90 c. c.	0.0850 g.
10	19.89	0.0849
10	20.06	0.0856
10	19.92	0.0851
10	19.88	0.0849
		Average 0.0851

By McCay and Anderson's mercury reduction method. The same solution of permanganate as above was used, 0.0962 N.

Volume solution taken	$KMnO_4$ required	V_2O_5 found
10 c. c.	9.80 c. c.	0.0858 g.
10	9.73	0.0852
10	9.78	0.0856
10	9.80	0.0858
10	9.82	0.0860
		Average 0.0857

The next series of determinations was made iodometrically as follows: 10 c. c. of the standard vanadium solution were measured out in a 400 c. c. beaker. 2 or 3 grams of solid potassium iodide were added and stirred until dissolved. 5 c. c. of 6N. hydrochloric acid were then added, and after thorough mixing, the solution was diluted to 300 c. c. and titrated with 0.1013 N. thiosulphate.

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	9.30 c. c.	0.0857 g.
10	9.29	0.0856
10	9.23	0.0851
10	9.33	0.0860
10	9.32	0.0858
10	9.30	0.0857
10	9.31	0.0858
10	9.31	0.0858
10	9.33	0.0860
10	9.24	0.0852
10	9.23	0.0851
10	9.25	0.0853
20	18.55	0.1710
20	18.60	0.1714
30	27.80	0.2563
	Average (10 c. c.)	0.0856

Another series using a thiosulphate solution 0.06266 N. gave these results:

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	15.02 c. c.	0.0856 g.
10	15.00	0.0855
10	15.02	0.0856
10	15.00	0.0855
10	14.95	0.0853
10	14.88	0.0848
	Average	0.0854

Same, using a 0.0623 N. thiosulphate solution.

10	15.08	0.0856
10	15.06	0.0854
10	15.06	0.0854
10	15.11	0.0857
	Average	0.0855

All of the above determinations were made paying no particular attention to the amount of potassium iodide added, the amount of acid present, or the time of standing before dilution. In the following determinations, strict attention was paid to these factors. In all cases a 0.04688 N. thiosulphate solution was used.

In the following determinations, 2 g. of potassium iodide and 5 c. c. of 6N. hydrochloric acid were added to 10 c. c. of the vanadium solution, after which the solution was diluted and titrated immediately.

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	20.12 c. c.	0.0858 g.
10	20.17	0.0860
10	20.08	0.0856
10	20.15	0.0859

Same as above, using 10 c. c. of hydrochloric acid instead of 5 c. c.

10	20.17	0.0860
10	20.16	0.0860

Using 5 c. c. of 6N. hydrochloric acid and 4 g. potassium iodide. No standing before diluting.

10	20.14	0.0859
10	20.18	0.0860
10	20.17	0.0860
10	20.15	0.0859
10	20.14	0.0859
10	20.14	0.0859

Using 10 c. c. of 6N. hydrochloric acid and 4 g. of potassium iodide. No standing before diluting and titrating.

20	40.31	0.1719
20	40.27	0.1716

5 c. c. of 6N. hydrochloric acid and 2 g. of potassium iodide were added to the vanadium solution. After standing 5 minutes the solution was diluted and titrated. The following results were obtained:

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	20.03 c. c	0.0854 g.
10	20.00	0.0853
10	20.07	0.0856

Same as above, except that 4 g. of potassium iodide were added.

10	20.09	0.0857
10	20.09	0.0857

2 g. potassium iodide and 5 c. c. 6N. acetic acid. After standing 1 minute, the solution was diluted and titrated.

10	1.35	0.0057

2 g. potassium iodide, and 1 or 2 c. c. 6N. hydrochloric acid. One minute standing before dilution.

10	19.21	0.0819
10	19.31	0.0824

4 g. potassium iodide, and 2 c. c. of 6N. hydrochloric acid. One minute standing before diluting.

10	20.06	0.0856

2 g. potassium iodide, and 1 c. c. 6N. hydrochloric acid. 5 minutes standing before dilution.

10	19.95	0.0851

4 g .potassium iodide, and 1 c. c. of 6N. hydrochloric acid. 5 minutes standing before diluting.

Volume solution taken	$Na_2S_2O_3$ required	V_2O_5 found
10 c. c.	20.05 c. c.	0.0855 g.

Using 5 or 10 c. c. of 6N. sulphuric acid instead of hydrochloric acid.

10	20.12	0.0858
10	20.12	0.0858

The method was tested further using larger quantities of vanadium. Somewhat larger quantities of acid and potassium iodide were used in these determinations.

20	40.35	0.1721
20	40.36	0.1721
30	60.45	0.2579
30	60.42	0.2577
40	80.44	0.3432

In the presence of over 0.2 g. V_2O_5, the end point is not so sharp as is the case of smaller quantities, the reason being that the intense blue of the vanadyl compound masks the starch iodide blue somewhat. The end point is still sensitive to one drop of N/10 thiosulphate solution however.

Summary of Values Found of the Vanadium Content by Different Methods

A summary of the values obtained by the various methods for the vanadium content of 10 c. c. of the solution is as follows:

Mercury reduction method.	0.0848 ± 0.0002 g. V_2O_5
Iodometric method (0.1013 N. $Na_2S_2O_3$)	0.0855 ± 0.0003
Iodometric method (0.6266 N.)	0.0851 ± 0.0005
Iodometric method (0.0623 N.)	0.0857 ± 0.0005
Iodometric method (0.04688 N.)	0.0856 ± 0.0005
Zinc reductor method (series I.)	0.0854 ± 0.0004
Zinc reductor method (series II.)	0.0855 ± 0.0002
Holverscheit's method.	0.0858 ± 0.0005

The Iodometric Determination of Pure Vanadium Pentoxide

The method was tested out further using some especially purified V_2O_5 as a standard. This was prepared by twice recrystallizing ammonium vanadate from hot water, drying the resulting product in the air, and converting it into the pentoxide by heating in a porcelain dish to 400° C. in a muffle furnace. The residue was moistened with pure nitric acid, and again heated to 400° C. This treatment was repeated once more. The resulting product was a uniform yellowish orange powder. It was preserved in a stoppered weighing bottle, and portions were weighed out as needed.

This material was completely soluble in ammonium hydroxide, and in dilute solutions of sodium bicarbonate and sodium hydroxide. 0.2738 g. of it, when heated to fusion in a porcelain crucible, lost 0.0008 g. or about 0.3%. To test the purity, weighed amounts of the material were dissolved in hot concentrated sulphuric acid. The resulting solutions were diluted, and the vanadium determined by the zinc reductor method. The permanganate used was 0.0962 N., and the "blank" on the reductor was 0.2 c. c. The following results were obtained.

V_2O_5	$KMnO_4$—blank	V_2O_5 found	Difference
0.0499 g.	17.20 c. c.	0.0502 g.	+0.0003 g.
0.0707	24.07	0.0702	—0.0005
0.0794	24.27	0.0796	+0.0002
0.1424	48.75	0.1423	—0.0001

The purity was tested further by the mercury reduction method. The permanganate used was 0.1098 N.

0.0794	7.95	0.0794	0.0000
0.0759	7.63	0.0762	+0.0003
0.0766	7.64	0.0763	—0.0003

Determinations by the iodometric method on this material were then made as follows: Since preliminary determinations pointed to the fact that the vanadium was not entirely in the pentavalent condition, it was necessary to first convert any reduced vanadium to the fully oxidized condition. It was found that approximately 1% of the vanadium was present in the vanadyl state. The most satisfactory method of oxidation was found to be that of boiling the alkaline solution with hydrogen peroxide.

Weighed portions of the vanadium pentoxide were dissolved in a few c. c. of sodium hydroxide solution, and treated with a small amount of hydrogen peroxide. (In some cases, the vanadium was dissolved in sodium peroxide and water.) The excess hydrogen peroxide was then expelled by boiling. When hydrogen peroxide is first added to an alkaline solution of a vanadate, a yellow coloration appears. This disappears when the solution is boiled. Complete expulsion of the excess hydrogen peroxide was always found when the boiling was continued a few minutes longer than necessary to completely decolorize the solution. The solution was cooled, treated with a gram or two of potassium iodide, acidified with 5 or 10 c. c. of dilute hydrochloric acid, diluted to about 300 c. c., and titrated with 0.0623 N. thiosulphate. The following results were obtained.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0117 g.	2.08 c. c.	0.0118 g.	+0.0001 g.
0.0335	5.93	0.0336	+0.0001
0.0458	8.14	0.0461	+0.0003
0.0485	8.67	0.0491	+0.0006
0.0739	13.04	0.0740	+0.0001
0.0979	17.25	0.0978	—0.0001
0.1495	26.28	0.1492	—0.0003
0.1566	27.71	0.1571	+0.0005
0.1735	30.67	0.1740	+0.0005
0.1736	30.58	0.1733	—0.0003
0.1871	32.92	0.1868	—0.0003
0.2365	41.60	0.2360	—0.0005
0.2381	42.01	0.2384	+0.0003

This demonstrates the accuracy of the method.

The Oxidization of Vanadium to the Pentoxide

To obtain satisfactory results with the above method, it is essential that the vanadium be first oxidized to the pentavalent condition. In the prosecution of this work, it was found that this was often a difficult problem, as vanadium is very susceptible to reduction.

As has been mentioned before, the solid vanadium pentoxide used was found to be partly in the vanadyl condition. This is shown by the following experiments. Weighed portions of the material were dissolved in a few c. c. of sodium bicarbonate solution. Potassium iodide and hydrochloric acid were then added, and the solution was diluted and titrated in the usual manner. The thiosulphate used was 0.1013 N.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0666 g.	7.20 c. c.	0.0664 g.	—0.0002 g.
0.1168	12.57	0.1158	—0.0010
0.1253	13.44	0.1239	—0.0014
0.0427	4.60	0.0424	—0.0003

The following portions were dissolved in 3 c. c. of concentrated sulphuric acid, diluted with a little water, treated with potassium iodide, and the titrations finished as usual.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0940 g.	10.08 c. c.	0.0929 g.	—0.0011 g.
0.0821	8.78	0.0809	—0.0012
0.1682	18.00	0.1659	—0.0023
0.0853	9.11	0.0840	—0.0013

These results indicate that the sample contained about 1% of the vanadium in the vanadyl state of oxidation.

It was next attempted to oxidize the vanadium by boiling the acid solution with bromine water. Weighed portions of the sample were dissolved in sodium bicarbonate solution. The solution was acidified with 5 c. c. of concentrated sulphuric acid. 10 c. c. of bromine water were added, and the solution was boiled until the excess bromine had been completely expelled. The solution was cooled, and the vanadium determined as usual by the iodometric method, using 0.0623 N. thiosulphate.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.1052 g.	18.20 c. c.	0.1033 g.	—0.0019 g.
0.0536	9.48	0.0538	+0.0002
0.1600	28.00	0.1589	—0.0011
0.0821	13.86	0.0786	—0.0035

These results indicate that oxidation by means of bromine water in acid solution is not satisfactory.

During the progress of the work, several points were brought out regarding the susceptibility of vanadium pentoxide to reduction. For instance when 10 c. c. portions of the standard vanadium solution were boiled down to about 2 c. c., and the vanadium determined iodometrically in the usual manner, the following results were obtained. The thiosulphate used was 0.04688 N.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0856 g.	19.68 c. c.	0.0839 g.
0.0856	19.98	0.0851
0.0856	19.87	0.0847

Other portions were evaporated to dryness, taken up in hydrochloric acid and water, and finished as above.

0.0856	19.80	0.0845
0.0856	19.85	0.0847
0.0856	20.17	0.0860
0.0856	19.68	0.0839
0.0856	19.92	0.0850
0.0856	19.26	0.0821
0.1712	39.70	0.1693

These low results may be explained by the fact that the standard vanadium solution contained a small amount of hydrochloric acid. It had been prepared by dissolving vanadium pentoxide in a sodium bicarbonate solution, neutralizing the excess bicarbonate with a small amount of hydrochloric acid. Sufficient hydrochloric acid was apparently present, however, to partially reduce the vanadium in the above treatment.

This is further exemplified by the following experiments. The vanadium solution was treated with 2 c. c. of concentrated sulphuric acid, and evaporated to fumes of sulphur trioxide. The solution was then diluted with a little water, and the vanadium determined as usual, using 0.1013 N. thiosulphate.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0856 g.	9.12 c. c.	0.0841
0.0856	8.97	0.0817

The following determinations were also brought to sulphur trioxide fumes, after which a little nitric acid was added, and the solution brought to fumes again.

0.0856	9.10	0.0839
0.0856	9.12	0.0841
0.0856	9.10	0.0839
0.0856	9.10	0.0839

It was later found that by merely fuming a sulphuric acid solution of a vanadate for some time, some of the vanadium may be reduced. This fact has also previously been noted by Cain and Hostetter[98], who found that 8 mg. of V_2O_5, when fumed with 15 or 20 c. c. of sulphuric acid in a covered flask for 4 or 5 hours, was practically completely reduced to V_2O_4.

This is also shown by the following experiments in which weighed portions of the pure vanadium pentoxide were dissolved in sodium hydroxide solution. 5 c. c. of concentrated sulphuric and 5 c. c. of concentrated nitric acid were then added, and the excess nitric acid removed by evaporation on the steam bath. The solutions were diluted with a little water, cooled, treated with potassium iodide, and titrated as usual, using 0.0507 N. thiosulphate.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0295 g.	5.84 c. c.	0.0269 g.	—0.0026 g.
0.0822	16.80	0.0775	—0.0047
0.0347	6.65	0.0307	—0.0040

Two other samples of the same batch were heated over a free flame to sulphur trioxide fumes, and the titration finished as above.

0.0704	13.97	0.0645	—0.0059
0.1062	21.59	0.0996	—0.0066

The above determinations were repeated using 5 c. c. of phosphoric acid instead of sulphuric acid. The following results were obtained. The thiosulphate was 0.0507 N.

0.0224	4.82	0.0222	—0.0002
0.0389	8.32	0.0384	—0.0005
0.0655	14.04	0.0648	—0.0007
0.0971	20.87	0.0963	—0.0008
0.1427	30.68	0.1416	—0.0011

Same using 0.0623 N. thiosulphate.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0537 g.	9.31 c. c.	0.0528 g.	—0.0009 g.
0.1201	20.90	0.1185	—0.0016

[98] J. Ind. En. Chem. 4, 252 (1912).

These results indicate that vanadium cannot be satisfactorily oxidized with nitric acid in the presence of sulphuric acid. With phosphoric acid, better results are possible, but still not entirely satisfactory.

The only really satisfactory method for the oxidation was the use of hydrogen peroxide in alkaline solution. This has been shown in a previous section of this paper. The fact that hydrogen peroxide can be completely expelled by boiling the sodium hydroxide solution is shown by the following determinations on the standard vanadium solution. 10 c. c. portions of the solution were treated with a little sodium hydroxide, and 5 c. c. of hydrogen peroxide, boiled to decompose the peroxide, and then treated with potassium iodide and hydrochloric acid as usual. The thiosulphate solution used was 0.0623 N.

0.0856	15.09	0.0856	0.0000
0.0856	15.05	0.0854	—0.0002
0.0856	15.01	0.0852	—0.0004

The Effect of Dilution on the Results

Some work on more dilute solutions resulted as follows: 10 c. c. of the standard vanadium solution was diluted to 30 c. c. with water. The resulting solution was then treated with hydrochloric acid and potassium iodide, diluted and titrated with 0.04688 N. thiosulphate.

V_2O_5 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0856 g.	20.41 c. c.	0.0870 g.
0.0856	20.42	0.0870
0.0856	20.55	0.0876

Another 10 c. c. portion of the vanadium solution was diluted to 100 c. c., potassium iodide and 10 c. c. of concentrated hydrochloric acid were added, and the solution was allowed to stand for 4 minutes. It was then diluted to 300 c. c. and titrated. 15.52 c. c. of 0.0623 N. thiosulphate solution were required, corresponding to 0.0880 g. V_2O_5. The end point was very fleeting, however, as the blue color returned almost at once, and continued to come back rapidly even when repeatedly decolorized by the addition of a few more drops of thiosulphate.

Summary

Vanadium may be determined very accurately iodometrically provided the proper precautions are taken. The sharpness of the endpoint, and the ease of carrying out the process leave little to be desired. The chief difficulty seems to be in getting all of the vanadium oxidized to the pentavalent condition at the start. If the additional precaution of having a low initial volume is adhered to, and a reasonable excess of either hydrochloric or sulphuric acid is present, no difficulty should be experienced in obtaining accurate results.

The total volume after addition of the acid and potassium iodide should not exceed 20 c. c. Any strong mineral acid is satisfactory; hydrochloric or sulphuric are the best. Phosphoric acid may be used, but in this case the solution should be allowed to stand a few minutes before dilution to allow the reaction to go to completion. It seems to make no difference whether the acid or the iodide are added first. After both have been added, the solution may be diluted to any convenient volume for titration.

Since the method, when the proper precautions are taken, is satisfactory when vanadium is present alone, the next step was to find out if other elements inter-

fered with the process. Accordingly, mixtures of vanadium with molybdenum, tungsten, and uranium were prepared and treated in the usual manner.

The Iodometric Determination of Vanadium in Presence of Molybdenum

Weighed portions of vanadium pentoxide were dissolved in a small amount of sodium bicarbonate solution, and to the resulting solution was added 25 c. c. of a standard solution of ammonium molybdate containing 0.2004 g. of MoO_3. The mixture was evaporated to low volume on the steam bath; a small amount of sodium peroxide was added, and the solution boiled to decompose the excess peroxide. The solution was cooled, potassium iodide was added, and the solution was acidified with 10 c. c. of concentrated hydrochloric acid. The solution was diluted at once to 300 c. c., and titrated with 0.0623 N. thiosulphate.

V_2O_5 taken	MoO_3 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0605 g.	0.2004 g.	10.93 c. c.	0.0620 g.
0.0800	0.2004	17.81	0.1010 .
0.1045	0.2004	19.13	0.1085
0.1626	0.2004	29.02	0.1646

The end points were not very permanent. The shading of the deep blue starch iodide color to the pale blue vanadium was more gradual than in the case where vanadium was present alone. The end points kept returning even when the blue color was repeatedly decolorized with thiosulphate.

A blank on 25 c. c. of the molybdenum solution containing 0.2 g. MoO_3, by adding potassium iodide and 10 c. c. of concentrated hydrochloric acid, gave a titration value of 0.2 c. c. of 0.0623 N. thiosulphate. A similar blank which was allowed to stand for 2 minutes after adding potassium iodide and hydrochloric acid, but before diluting, required 0.33 c. c. of this thiosulphate solution. The end points seemed quite permanent.

A blank similar to the above, replacing the hydrochloric acid with 5 c. c. of phosphoric acid, gave no coloration with starch solution. Bearing this in mind, a second series of vanadium-molybdenum mixtures were prepared, and the vanadium was determined as before, replacing the hydrochloric acid by 5 or 10 c. c. of phosphoric acid. The following results were obtained. 0.0623 N. thiosulphate was used.

V_2O_5 taken	MoO_3 taken	$Na_2S_2O_3$ used	V_2O_5 found	Difference
0.0295 g.	0.0925 g.	5.22 c. c.	0.0296 g.	+0.0001 g.
0.0402	0.2050	7.05	0.0400	—0.0002
0.0594	0.1925	10.39	0.0590	—0.0004
0.0832	0.0457	14.64	0.0831	—0.0001
0.1259	0.4021	21.95	0.1245	—0.0014
0.1579	0.2324	27.75	0.1575	—0.0004

The end points were satisfactory, although not as permanent as in the case where vanadium alone was present.

These results indicate that vanadium may be determined iodometrically in the presence of molybdenum if phosphoric acid is used instead of hydrochloric.

Two explanations may be offered for the better results obtained when phosphoric acid is used. Possibly phosphoric acid is so much weaker as an acid than hydrochloric acid that the reaction between the molybdate and hydriodic acid does

not take place to an appreciable extent; or the molybdenum may be tied up as a complex phosphomolybdate, and rendered inactive in this way.

The Iodometric Determination of Vanadium in the Presence of Tungsten

Weighed portions of vanadium pentoxide and tungsten trioxide (see footnote) were dissolved in water and sodium peroxide, and the excess peroxide was destroyed by boiling. Potassium iodide was added, then 5 c. c. of concentrated hydrochloric acid, and the solution was diluted and titrated as usual. 0.0623 N. thiosulphate was used.

V_2O_5 taken	WO_3 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0471 g.	0.1514 g.	8.16 c. c.	0.0463 g.	—0.0008 g.
0.0497	0.0250	8.71	0.0494	—0.0003
0.0553	0.1478	9.68	0.0549	—0.0004
0.1136	0.0635	19.98	0.1134	—0.0002
0.1685	0.0685	29.52	0.1675	—0.0010
0.2109	0.2666	36.93	0.2095	—0.0014

When the solutions were acidified, a white precipitate separated. Possibly this precipitate may have occluded enough vanadium to make the results slightly low.

In the presence of tungsten, the iodometric method seems to give slightly low results for vanadium.

The Iodometric Determination of Vanadium in the Presence of Uranium

The presence of uranium interferes considerably with the iodometric determination of vanadium. Although uranium does not itself reduce potassium iodide, as shown by a blank, it interferes with the oxidation of vanadium in alkaline solution with hydrogen peroxide. A blank of about 0.5 grams of uranyl acetate, when dissolved in a little water, and treated with potassium iodide and hydrochloric acid, gave no blue color when starch solution was added. When an acid solution of vanadium and uranium is made alkaline with sodium peroxide however, a precipitate of uranyl vanadate is formed, and at the same time a higher oxide of uranium may be formed which is difficult to decompose by boiling. If the solution is made acid with hydrochloric acid and boiled to decompose the excess peroxide, part of the vanadium may be reduced by the hydrochloric acid. If sulphuric acid is used and the solution is boiled, the hydrogen peroxide may reduce part of the vanadium if the solution is of low volume.

V_2O_5 taken	U_3O_8 taken	$Na_2S_2O_3$ required	V_2O_5 found	Difference
0.0684 g.	0.216 g.	13.41 c. c.	0.0760 g.	+0.0076 g.
0.1638	0.384	26.50	0.1502	—0.0136
0.1423	0.356	23.87	0.1352	—0.0071
0.1020	0.064	17.95	0.1017	—0.0003

The titration was made with 0.0623 N. thiosulphate.

The above results were obtained as follows: Mixtures of vanadium pentoxide and uranyl acetate were dissolved in water and sodium bicarbonate. Sodium peroxide was added and the solution was boiled. A precipitate appeared shortly

The tungsten trioxide used in these experiments had been purified by Mr. F. A. Gray in the analytical chemical laboratory at the University of Minnesota.

after the boiling commenced. After boiling for some time, the determinations were finished individually as follows:

Number 1 was acidified with hydrochloric acid, and gave a distinct red coloration due to the formation of pervanadic acid, showing the presence of hydrogen peroxide. When treated with potassium iodide, diluted and titrated, the high result obtained was due to the presence of hydrogen peroxide.

Number 2 was acidified with hydrochloric acid, and boiled to decompose the hydrogen peroxide. The solution became greenish tinged during the boiling, indicating some reduction of the vanadium. This explains the low result.

Numbers 3 and 4 were acidified with sulphuric acid, and boiled to decompose the hydrogen peroxide. Even here the reducing effect of the peroxide in the presence of sulphuric acid is shown in number 3, although number 4 is satisfactory.

The following results obtained by adding weighed amounts of uranyl acetate to a measured quantity of a standard vanadium solution. 5 c. c. of dilute hydrochloric acid were added, and the solution was shaken to dissolve the uranium acetate. Potassium iodide was then added, and the solution was diluted and titrated. 0.0505 N. thiosulphate was used.

V_2O_5 taken	U_3O_8 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0657 g.	0.093 g.	14.34 c. c.	0.0659 g.
0.0657	0.145	14.33	0.0658
0.0657	0.167	14.33	0.0658
0.0657	0.332	14.32	0.0658
0.1314	0.354	28.70	0.1319

These results indicate that uranium does not liberate iodine from potassium iodide in the presence of vanadium. The difficulty in the iodometric estimation of vanadium in the presence of uranium comes, then, in its interference in the oxidation of vanadium in alkaline solution with hydrogen peroxide.

The Titration of Vanadious Salts With Potassium Iodate

It is a well established fact that when an acid solution of a vanadate is passed through a column of zinc, it is reduced to the divalent condition. In this state the vanadium is very susceptible to oxidation by the air, and it is even said to decompose water, liberating hydrogen, since it is such an active reducing agent. The common method to prevent this is to catch the reduced solution in a solution of ferric alum, which oxidizes the vanadium to the tetravalent condition, and itself becomes reduced to the ferrous condition. The resulting solution is titrated with permanganate at 70° C.

A few experiments were conducted by running the vanadium solution through a column of zinc, and catching the reduced solution in a measured amount of standard potassium iodate solution. It was hoped that this would oxidize the vanadium to the tetravalent condition, according to the following reaction.

$$3V_2O_2 + 2KIO_3 = 3V_2O_4 + 2KI.$$

The excess potassium iodate could then be determined by adding potassium iodide, and titrating the iodine liberated with thiosulphate. If this were possible, it was hoped further that the titration could be performed in the presence of ferrous iron without interference of the latter.

Accordingly solutions of sodium thiosulphate and potassium iodate were standardized against each other. The thiosulphate had been previously standardized against resublimed iodine, and against a standard permanganate solution.

Some preliminary experiments were made as follows: A solution of known vanadium content was diluted to about 100 c. c., acidified with 5 c. c. of concentrated hydrochloric acid, and heated to 50° C. It was then passed through a column of zinc and caught in a slight excess of standard potassium iodate solution. As the reduced vanadium solution came in contact with the iodate, the solution turned slightly yellow, due to liberated iodine. The reductor was washed with warm 2.5% hydrochloric acid, the solution was treated with excess potassium iodide, and the iodine liberated was titrated with standard thiosulphate solution to the pale vanadyl blue, using starch indicator. 0.1004 N. potassium iodate, and 0.0521 N. thiosulphate were used. The following results were obtained.

V_2O_5 taken	KIO_3 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0982 g.	25.00 c. c.	6.69 c. c.	0.0984 g.
0.0982	25.58	7.70	0.0986
0.0982	25.45	7.38	0.0988
0.0982	24.26	5.71	0.0973
0.0982	27.14	10.54	0.0985
0.0982	27.46	11.31	0.0986
0.1964	49.65	12.62	0.1969
0.2946	73.88	21.38	0.2867
0.2946	74.93	20.62	0.2934

These results were calculated without correcting for a blank on the reductor, which was later found to be equivalent to about 0.15 c. c. of N/20 potassium iodate, or equivalent to 0.0003 g. V_2O_5.

Unfortunately, later determinations failed to check the results in the above table.

A blank, run on the reductor, by passing through it about 400 c. c. of warm 2.5% hydrochloric acid solution, catching in a measured volume of iodate solution, treating with potassium iodide and titrating, gave these results. The iodate used was 0.05022 N. and the thiosulphate was 0.05211 N.

KIO_3 taken	$Na_2S_2O_3$ required	Blank (in terms of KIO_3)
41.27 c. c.	39.65 c. c.	0.15 c. c.
43.01	41.37	0.11
45.90	44.13	0.14
44.96	43.15	0.21

Same using sulphuric acid instead of hydrochloric.

40.35	38.76	0.13
39.20	37.64	0.14
39.03	37.50	0.12
39.98	38.40	0.14

Another series of vanadium determinations, using sulphuric acid instead of hydrochloric, resulted as follows: The iodate was 0.0502 N. and the thiosulphate was 0.0522 N. A blank of 0.15 c. c. of iodate was also subtracted.

V_2O_5 taken	KIO_3 taken	$Na_2S_2O_3$ required	V_2O_4 found
0.0982 g.	46.15 c. c.	6.10 c. c.	0.0906 g.
0.0982	47.35	6.42	0.0926
0.0982	49.38	7.60	0.0945

When a standard solution of potassium bromate was substituted for the iodate the following results were obtained. 25.00 c. c. of the bromate were found to require 47.99 c. c. of 0.0521 N. thiosulphate. No blank was used.

V_2O_5 taken	$KBrO_3$ taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0982 g.	25.00 c. c.	5.80 c. c.	0.1000 g.
0.0982	25.00	5.58	0.1004

Several more determinations were then made using 0.0502 N. potassium iodate in the receiving flask, and titrating with 0.0522 N. thiosulphate. A blank of 0.15 c. c. iodate was subtracted from the total amount used. Hydrochloric acid was used in all cases. The following results were obtained:

V_2O_5 taken	KIO_3 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0982 g.	49.62 c. c.	6.50 c. c.	0.0977 g.
0.0982	49.53	6.50	0.0975
0.0982	49.70	6.89	0.0970
0.0982	63.40	20.00	0.0972
0.0982	48.66	6.06	0.0967
0.0982	49.37	6.66	0.0967
0.0982	50.02	7.00	0.0974
0.0982	47.70	5.59	0.0954
0.0982	48.85	6.00	0.0971
0.0982	48.92	6.20	0.0968
0.0982	48.30	5.32	0.0963
0.0982	49.03	6.20	0.0970
0.0982	49.86	6.76	0.0974
0.1964	92.25	7.25	0.1933

Same using 0.09156 N. iodate and 0.0507 N. thiosulphate.

V_2O_5 taken	KIO_3 taken	$Na_2S_2O_3$ required	V_2O_5 found
0.0770 g.	40.83 c. c.	40.76 c. c.	0.0761 g.
0.1219	46.18	32.38	0.1177
0.1024	41.17	31.09	0.1000
0.0382	26.03	30.90	0.0372

These 4 calculations were made without subtracting the blank. These results run from 0.5 mg. to 4.0 mg. V_2O_5 too low, and hence the method is not satisfactory.

To determine how iron would behave under these conditions, several determinations similar to the above were made replacing the vanadium solution with a N/10 solution of ferrous sulphate. A measured amount of the iron solution was acidified with hydrochloric acid and passed through the reductor in the usual manner, catching the reduced solution in a measured amount of standard iodate. After washing out the reductor, the solution was treated with potassium iodide, and the iodine liberated was titrated with thiosulphate. Irregular results were obtained, but some iron was probably oxidized in every case.

$FeSO_4$ taken	KIO_3 taken	$Na_2S_2O_3$ required	KIO_3 reduced
N/10 sol.	0.0502 N.	0.0522 N.	by the Fe
25 c. c.	38.94 c. c.	36.11 c. c.	1.29 c. c.
25	41.50	39.11	0.94
25	22.80	21.62	0.37
100	23.66	14.08	9.58
100	21.70	16.66	4.42

In all these determinations a transient end point was obtained, the starch blue returning after about one minute's standing. The iron is apparently slightly oxidized under these conditions, but may be partially reduced later by the potassium iodide.

When a standard solution of iodine was used in the receiver instead of potassium iodate, a much higher blank was obtained. The iodine solution was prepared by treating a measured amount of standard iodate in the receiver with potassium iodide and hydrochloric acid. About 300 c. c. of warm 2.5% hydrochloric acid solution was then passed through the reductor, and the resulting solution titrated with standard thiosulphate. Three determinations gave blanks of 0.35 c. c., 1.74 c. c., and 2.23 c. c. of 0.0502 N. KIO_3 respectively. Under these conditions, some iodine may have been lost by volatilization.

Jamieson[56] has shown that when an acid solution of a molybdate is passed through a zinc reductor, and the reduced solution is caught in iodine monochloride, the resulting solution may be titrated with standard potassium iodate, under which condition the molybdenum is reoxidized to Mo_2O_5 at once, or to MoO_3 very slowly, the latter reaction requiring about two days for completion. The titration must be carried out in the presence of considerable hydrochloric acid to prevent the hydrolysis of the iodine monochloride formed during the titration.

It would be interesting then to see what would happen when a molybdenum solution was treated in a manner similar to the vanadium above. A warm solution of known molybdenum content containing about 5% of hydrochloric acid was passed through a zinc reductor and caught in a measured volume of standard potassium iodate. After washing out the reductor in the usual way, the solution was treated with potassium iodide and titrated with standard thiosulphate solution. The following results were obtained.

MoO_3 taken	KIO_3 taken	$Na_2S_2O_3$ required	MoO_3 found	
	0.0915 N.	0.1013 N.	(1)	(2)
0.0799 g.	25.00 c. c.	10.40 c. c.	0.0594 g.	0.0890 g.
0.0799	25.00	10.35	0.0596	0.0894
0.0799	25.00	10.50	0.0589	0.0884
0.0799	25.00	10.11	0.0607	0.0910
0.1598	50.00	19.51	0.1250	0.1872

In the above table the results in the column "MoO_2 found (1)" are based on the oxidation of Mo_2O_3 to MoO_3, while those in the "MoO_3 found (2)" column are calculated on the basis of the oxidation of Mo_2O_3 to Mo_2O_5. This indicates that the oxidation proceeds to some intermediate point between Mo_2O_5 and MoO_3. The end point of this titration is very sharp, the color changing from a deep blue to a clear yellow.

Conclusion

The conclusion to be drawn from these experiments is that this method, even if it were developed to be satisfactory for vanadium, would not be satisfactory in the presence of iron and molybdenum, and it would therefore be no improvement over the original method of catching the solution in ferric alum, and titrating with permanganate. The only advantage would be the slightly sharper end point possible by this method.

The Attempted Use of Cupferron to Separate Vanadium from Molybdenum

Cupferron as a reagent for precipitating vanadium was first mentioned by Rodeja[6]. Turner[15] found the precipitation to be complete in a solution containing 1% of either sulphuric or hydrochloric acid, using a slight excess of a 6% solution of cupferron in water as the reagent.

Determinations on a known quantity of vanadium resulted as follows: 10 c. c. of a standard vanadium solution were diluted to 150 c. c., and sufficient sulphuric acid was added to give a 1% acidity. A 6% solution of cupferron was then added until precipitation was complete. The precipitate was filtered at once using suction, and washed with 1% sulphuric acid containing 1.5 g. of cupferron per liter. The precipitate and paper were ignited to constant weight in platinum. The following results were obtained.

V_2O_5 taken	V_2O_5 found
0.0982 g.	0.0972 g.
0.0982	0.0972
0.0982	0.0973
0.0982	0.0972

A small amount of vanadium was found in one of the filtrates by adding nitric acid and evaporating to fumes of sulphur trioxide to oxidize the organic matter, and testing with hydrogen peroxide. This explains the low results. The question of why the vanadium was not completely precipitated was not investigated further, since in subsequent determinations in which molybdenum was also present, the molybdenum was found to interfere to such an extent as to render the method useless for a separation of the two elements.

Determinations similar to the above, but containing molybdenum, gave these results:

V_2O_5 taken.	MoO_3 taken.	Weight of resulting precipitate.
0.0982 g.	0.0802 g.	0.1497 g.
0.0982	0.0802	0.1569
0.0982	0.0802	0.1562
0.1533	0.2004	0.2163
0.1533	0.2004	0.1588
0.0428	0.0401	0.0741

None of these precipitates were ignited to constant weight, since molybdenum was shown to be present in every case by the sublimate of molybdenum trioxide that formed when the precipitate was fused. For instance, the first precipitate lost 10 mg. between two heatings.

Therefore this method of separating vanadium from molybdenum is useless since large quantities of the molybdenum are precipitated along with the vanadium. Just how completely the molybdenum was precipitated under these conditions was not investigated.

The Attempted Separation of Vanadium from Molybdenum by Boiling Their Slightly Acid Solutions with Zinc Oxide.

Briefs[97] obtained a quantitative separation of vanadates from chromates by boiling their slightly acid solution with an excess of zinc oxide. The precipitate contains all of the vanadium and only a small amount of the chromium. A complete separation is made by dissolving the precipitate in sulphuric acid, and again boiling the solution with zinc oxide. The second precipitate is free from chromium.

Some work was done to ascertain the behavior of molybdates under these conditions. A solution of ammonium molybdate containing 0.0799 g. of MoO_3 was diluted to 200 c.c., and treated with 5 c.c. of dilute sulphuric acid and an excess of zinc oxide. The solution was then boiled for 10 minutes. The insoluble matter was filtered off and washed with hot water. The filtrate was acidfied with sulphuric acid, and the precipitate was dissolved in dilute sulphuric acid. The amount of molybdenium present in each solution was then determined by the zinc reductor method with the following results:

MoO_3 found in the precipitate		0.0657 g.
MoO_3 found in the filtrate		0.0145
	Total	0.0802 g.
MoO_3 taken (total)		0.0799 g.

A mixture of 0.0799 g. MoO_3 and 0.0856 g. V_2O_5 were diluted to 200 c.c., acidified with sulphuric acid, and boiled 10 minutes with excess zinc oxide. The precipitate was filtered off and washed with hot water. The filtrate, when acidified with sulphuric acid and passed through a zinc reductor, and titrated with permanganate was found to contain 0.0259 g. MoO_3.

Conclusion

The separation of vanadium from molybdenum by boiling their slightly acid solution with zinc oxide is not possible, since most of the molybdenum is precipitated with the vanadium.

Summary

The temperature at which molybdenum trioxide begins to sublime has been determined.

It has been shown that molybdenum sulphide can be satisfactorily ignited to the oxide in the air.

In the separation of molybdenum from vanadium as sulphide, the most satisfactory procedure is to pass hydrogen sulphide into the acid solution, and precipitate the molybdenum with increased pressure. Some vanadium is always carried down with the molybdenum when the precipitation is made by acidifying the ammonium sulphide solution of the thio salts containing tartrates.

An iodometric method for the determination of vanadium has been developed.

[97] Stahl u. Eisen 42, 275 (1922).

Certain proposed methods for the separation of molybdenum from vanadium have been shown to be untrustworthy, thus simplifying the course of future research in this field.

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Vita

The author was born near Rochester, Minnesota, on February 27, 1897. His early boyhood was spent at Rochester, where he attended the grade and high schools, graduating from the latter in June, 1916. The following September he entered the School of Chemistry at the University of Minnesota, from which he received the degrees of Bachelor of Science in 1920 and Chemical Engineer in 1921.

From 1920 to 1923 he was Assistant in Analytical Chemistry at the University of Minnesota. The following year he was promoted to Instructor in the same department.

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In October, 1923, he published in the Journal of Industrial and Engineering Chemistry in conjunction with Paul H. M.-P. Brinton and Landon A. Sarver, an article on "The Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures Containing Small Amounts of Hydrofluosilicic Acid."